

Russian Original Vol. 28, No. 6, November-December, 1993

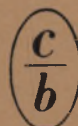
July, 1994

LITHOLOGY AND MINERAL RESOURCES

ЛИТОЛОГИЯ И ПОЛЕЗНЫЕ ИСКОПАЕМЫЕ

(LITOLOGIYA I POLEZNYE ISKOPAEMYE)

TRANSLATED FROM RUSSIAN



CONSULTANTS BUREAU, NEW YORK

LITHOLOGY AND MINERAL RESOURCES

Lithology and Mineral Resources is abstracted or indexed in *Chemical Abstracts*, *Engineering Index*, and *Metal Abstracts Index*.

Mailed in the USA by Publications Expediting, Inc., 200 Meacham Avenue, Elmont, NY 11003.

POSTMASTER. Send address changes to *Lithology and Mineral Resources*, Plenum Publishing Corporation, 233 Spring Street, New York, NY 10013.

Lithology and Mineral Resources is a translation of *Litologiya i Poleznye Iskopaemye*, a publication of the Russian Academy of Sciences.

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Subscription (6 Issues):

Vol. 28: \$1150 (domestic); \$1345 (foreign) Single issue: \$200
Vol. 29: \$1195 (domestic); \$1395 (foreign) Single Article: \$12.50

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233 Spring Street
New York, New York 10013

Lithology and Mineral Resources (0024-4902/93/\$12.50). Published bimonthly by Consultants Bureau, a division of Plenum Publishing Corporation, 233 Spring Street, New York, NY 10013. Annual Subscription price is \$1195 (domestic) and \$1395 (foreign). Second-class postage paid at Jamaica, New York 11431.

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A translation of *Litologiya i Poleznye Iskopaemye*

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Volume 28, Number 6

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The Russian press date (podpisano k pechati) of this issue was 10/20/1993. Publication therefore did not occur prior to this date, but must be assumed to have taken place reasonably soon thereafter.

FACIAL AND FORMATION INVESTIGATIONS – THE FOUNDATION OF SYSTEMS ANALYSIS OF LEVELS OF ORGANIZATION OF SEDIMENTARY DEPOSITS (Toward a Theory of Formation Analysis)

P. P. Timofeev and V. I. Troitskii

UDC 551.7.022:552.1

On the basis of analysis and synthesis of various theories and ideas, and also of methods of studying sedimentary and volcanogenic-sedimentary deposits, the authors consider the numerous factors determining and directing processes of sedimentogenesis. The method of detailed, comprehensive, lithological and facial study of the sedimentary mantle of continental and oceanic blocks of the Earth that was previously developed on a broad genetic basis made it possible to solve many fundamental problems of their genesis. It is shown that formation analysis must be a continuation and deepening of facial analysis, which result in a higher level of systems analysis of the organization of knowledge of sedimentary deposits.

One of the basic methods of scientific research is systems analysis of natural objects and events in their hierarchic coordination and integrity. The levels of organization distinguished as integral systems differ qualitatively from each other, and their structure and development are governed by the action of laws (concepts, hypotheses, theories) specific to and characteristic of them alone. Extrapolation of them from one level to another requires extreme caution. This proposition is equally true of the classification of levels of organization of geological objects: intraatomic particle – atom – mineral – lithological type of sediment (lithotype) – genetic type of sediment (genotype) – facial type of sediment (facies) – formation* – association of formations. Their unusual complexity, significant number of levels of investigation, different theories and systems of concepts, indeterminacy of the relationships between methods of investigation and logical-theoretical principles of generalization, the frequent absence of clear boundaries between levels, different interpretations of the unity and interrelation of structural-material and genetic aspects of sedimentation, the multitude of direct and inverse, often mediated relationships, and many other factors significantly determine the status of the theory and give rise to an abundance of ideas about hierarchies of geological bodies, and the principles and methods of distinguishing and classifying them.

In this case, our attention is drawn to the fact that, in spite of differences in the ranking of geological bodies and concepts contributing to their definition, the majority of researchers in their own classifications proceed from the fundamental proposition of the reality of a hierarchic series of sedimentary material, each member of which is a qualitatively different level of organization and, simultaneously, a reflection of qualitatively different geological processes [4-7, 13, 15-19, 22, 23, 25-29].

The successes of science in the future, as V. I. Vernadskii emphasized [2], will be determined not so much by deeper development of already established directions as by their specialization in separate problems and subsequent development into new branches of science. Among them, we can rightly include ideas about landscapes and facies (sediments + the conditions of their development) and, in the near future, about a unified, comprehensive teaching about

**Formation* – a sedimentation geological body. By formation we mean a natural, large complex of facial types of sediments, paragenetically related by place and condition of development, confined to a certain paleotectonic structure, and corresponding to a certain stage of its tectonic development. By *facies* we mean a complex of physical-geographic conditions of the sedimentation environment, as a result of the existence of which paragenetically related genetic types of sediments were formed, and also the sediments themselves, possessing a certain combination of genetic traits (conditions + sediments) [17].

geological sedimentary formations. Having originated in the depths of Earth science, they not only synthesized the achievements and methods of lithology, tectonics, historical geology, paleontology and stratigraphy, petrology, geochemistry, geophysics, etc., but also simultaneously received recognition as new directions in geological science.

The methodology of genetic systems analysis of sedimentary deposits proceeds from the necessity of knowing the genesis of sediments, their facial and landscape nature, formations, and complexes of them, which must form the foundation for creating a teaching about geological sedimentary formations.

In 1939, N. S. Shatskii, in a report published in the form of expanded theses "On movement and development of the Earth's crust" [25], based on analysis of structures of the Earth's crust and associated complexes of sedimentary and volcanogenic—sedimentary rocks, first expressed thoughts about geological formations as an essentially new direction in geological science. N. S. Shatskii wrote that the future of geological science consists in the fact that solution of general problems of the geology of our country, as well as the planet as a whole, requires a good theory based on an all-encompassing, scientifically grounded, detailed interpretation of observed facts, and that we are still just in the very beginning of this process [27]. He believed that their analysis and synthesis must be approached comprehensively, thoroughly, with consideration of the whole diversity of natural processes, events, and phenomena. According to his deep conviction, in the future the method of formation analysis will be of great use to geological science and practice. Somewhat earlier, i.e., in 1954, N. S. Shatskii wrote: "I think that this is connected with the fact that it simultaneously combines *lithological, stratigraphic, and tectonic approaches* (here and below, the italics are ours — P. T., V. T.). And such a unified formation method must produce effective results" [26, p. 12]. Underestimation of the possibilities of interpreting developing geological processes, primarily the genesis of sediments and rocks, and explanation of the reasons determining their occurrence on this basis delays the time when the properties and conditions of behavior of formations can be predicted, thus retarding the solution of such an important part of practical activity as prediction of and purposeful prospecting for mineral resources.

The diversity of genetic peculiarities of sedimentation and the development of formations is reflected in the composition and scale of manifestation of sedimentary mineral resources, which made up no less than 75-80% of the total mineral raw material. Successes in predicting and prospecting for them are predetermined, to a significant extent, by the state of knowledge about metallogenic (minerogenic) specialization of formations for certain mineral resources characteristic of them alone, and about the position of deposits in the internal structure of typical formations. Lithological-facial and formation methods of regional and local prediction of and prospecting for deposits of mineral resources are developing on this genetic basis.

Recognition of the unity of structural-material and genetic aspects of sedimentation and the development of formations indicates the need to study not only the levels of organization of sedimentary material, but also, to an equal degree, the typification and classification of the geological processes that give rise to them. A central place in this problem is occupied by the question of the boundaries between sediments, facies, formations, and associations of them — that new quality formed as a result of the accumulation of quantitative traits that is responsible for a new level of organization of sedimentary material. The conditions of sedimentation and development of formations are also qualitatively different categories.

Sedimentological and lithogenetic aspects of the genetic approach to study of formations make it possible to reconstruct the conditions of their accumulation (genesis), to know the patterns of their composition and internal structure, and relations with other formations, and also to trace the peculiarities of their subsequent development and transformation. Underestimation of the role of facial investigations, and efforts to distinguish formation subdivisions empirically, directly by means of analysis of paleotectonic and paleoclimatic situations, i.e., without deep study of the genesis of sediments and their paragenesis, significantly reduce the effectiveness of reconstructions of sedimentation basins [20].

Among the many directions in study and classification of sedimentary deposits, the genetic principle seems to be the most promising. Considering the state of the theory, it is outlined in a general, basic form for now. However, even in this case, the possibilities are expanding in the field of interpretation of complex processes of mobilization of sedimentary material, its movement, differentiation, accumulation, and depostion of sediments in different facial landscapes, the development of which in time leads to establishment of formations.

As a result, the whole diversity of genetic types of sedimentary deposits was predetermined by the overall trend of changes in the type of paleotectonic structures, their geotectonic conditions, and paleogeography. Paleoclimate and the composition of the material entering into the sedimentation basin also have an enormous influence on the development of different types of sedimentary formations. However, it is not always taken into account that paleostructure, geotectonic conditions, and paleogeography, being categories of a higher order than paleoclimate and material, also predetermine and

direct the development of structural-material systems (minerals – formations). Actually, they all influence their origin and development, though to different degrees, and not directly, but indirectly, through their transformation into landscapes and paleogeographic sedimentation situations. Landscapes (facial landscapes) in the direct sense cement the unity of genetic and structural-material aspects of formation analysis, i.e., they form parageneses of facial types of sediments and, in the final analysis, geological formations and associations of them.

Such ideas expand the possibilities of distinguishing and typifying sedimentation situations and the genetic types of sediments, facies, and formations associated with them. In this case, their classifications are open and not limited to the strict boundaries of, unfortunately, still quite debatable ideas about paleoclimates, tectonic conditions, types of regions and stages of their development, sources of material, and their irreversible evolution as a whole.

Thus, the foundation of genetic principles and methods of studying sedimentary deposits is facial analysis and its subsequent development into formation synthesis. Formation investigations must necessarily be preceded by facial analysis [13, 16, 17].

In spite of the imperfection and contradictoriness of the conceptual base, most researchers see as the fundamental propositions of lithology such concepts as lateral zonality of sedimentary accumulations and their sequence in cross sections of the Earth's crust, expressed in a regular lateral succession of facies and formations (facial and formation zonality), and also their historical-geological sequence (succession of cycles (parageneses) of genetic and facial types of sediments, i.e., cyclicity). The most important qualities of each of the hierarchies under consideration are the lateral (chorostructural) and historical-geological (chronostructural) relations characteristic of them alone. Ideas about the genesis and facial determination of sediments (formations of them), and their intermittently continuous development have to be supplemented by N. M. Strakhov's propositions [16] about the need for clear delineation of accessory, rock-forming, and, finally, formation-developing processes and their factors, and also the ideas of A. L. Yanshina [28], Yu. A. Zhemchuzhnikov [5], and others about the irreversible evolution of sedimentation in the Earth's history.

At present, the study and classification of sediments (rocks) are carried out in two main directions: petrographic proper and petrogenetic (facial-petrographic). In petrographic classifications, sediments are considered as structural-material categories that are formalized to a significant degree, separated according to particle size and the nature of packing of components, the ratio of terrigenous, authigenic, and biogenic components, mineral composition, etc. Their use in reconstructions does not solve the problem posed, and the classifications themselves are auxiliary. The development of a genetic classification of sediments and rocks is a future concern. However, its fundamental principles are established in the ideas about petrogenesis, facial determination, and the zonality of sedimentation.

Landscape, being a unified genetic system controlling the overall course of sedimentation, is also organized by levels. In the general form, these ideas were first formulated in teaching about zones of nature [3], biogeochemical systems [1], genetic types of sediments [8], and physical-geographic landscapes and facies [7]. Later, they were further developed in the works of V. I. Popov, N. M. Strakhov, L. B. Rukhin, Yu. A. Zhemchuzhnikov, P. P. Timofeev, and others.

The fundamental propositions about the facial zonality of deposits have now been confirmed by many examples of study of the regular relationship between landscapes of watershed-eluvial spaces together with the slopes undercutting them, and accumulations in alluvial fans of temporary and permanent flows, alluvial valleys and plains, all the way to their boundaries with the final runoff bodies of water. Detailed classifications of coastal and equatorial sections of inland and marginal marine basins have been developed. The facial zonality of abyssal parts of the oceans is being studied.

With a systems approach to discrimination of facies and their nomenclature, they appear as fully determined, sharply outlined categories. In connection with this, we cannot agree with E. V. Shantser's statement [24] that a classification of facies constructed according to a strictly hierarchic principle has no great scientific significance. The completely equal validity propagandized by representatives of this direction for various systems of facial subdivision according to a very limited number of particular traits (petrographic, paleontological, geochemical, paleogeographic proper, etc.) will hardly make it possible to approach the development of a unified classification of facies. In reality, sedimentation is expressed in a diversity of manifestations of dynamic, geochemical, biogenic, paleotectonic, tectonic, geomorphological, geophysical, and many other processes. However, each of them only characterizes particular aspects of a unified process. This was precisely what D. V. Nalivkin placed at the foundation of the physical-geographic principles of facial analysis that he suggested. In subsequent works by Yu. A. Zhemchuzhnikov, V. I. Popov, P. P. Timofeev, and others, classifications were developed that take into account the hierarchic coordination of individual links of the landscape, as well as their interrelation in a lateral series and a historical-geological sequence. In this case, each of the landscapes and parts of them

are characterized by their own way of organization of sedimentation processes and their own polydynamics; they are distinguished by a strict pattern in the distribution of types of sedimentary accumulations.

At the same time, the actual manifestations of facies in specific cross sections are more diverse, more complexly constructed than follows from the classifications presently suggested. Peculiarities in the development of different parts of the sedimentation basin uniting them undoubtedly show up here. Therefore, it is extremely important to develop classifications of landscapes (facial series) in different structural and paleoclimatic types of sedimentation basins, each of which is specialized with respect to processes, as well as the set of facially determined accumulations, including mineral resources [21].

Systematic ideas that are presently developing about landscapes primarily as physical-geographic categories characterize sedimentation in a generalized form and at a qualitatively different level. Further successes in the development of facial (and formation) investigations, it seems to us, will consist primarily in deeper study of the processes of differentiation in various sedimentation basins, taking into account the balance of absolute masses of sedimentary material.

The methodological basis of such research should be one of the main fundamental propositions of lithology about the three-component** (terrigenous, biogenic, and chemogenic) composition of sedimentary rocks and formations. Actually, the basis of sedimentation is made up of dynamic, geochemical, and biogenic processes. Their development is governed by strict laws; they can be evaluated not only qualitatively, but also quantitatively and, in a number of cases, confirmed by experiments. Any type of sedimentary accumulations bears signs of these three aspects of sedimentation. Therefore, it is not a landscape as such that controls and predetermines the general course of sedimentation, but its three subsystems (dynamic, geochemical, and biogenic). The scales of their manifestation and their relationships with each other explain the occurrence of facial series of sediments that are monosedimentary in petrogenesis (terrigenous, carbonate, halmeic, etc.) and the formations created by them, as well as ones that are polysedimentary, but united by the common nature of sedimentation situations. The latter is especially important, since the overwhelming majority of sediments and formations is nothing other than various combinations of these three basic genetic components of sedimentary material.

The effect of the subsystems under consideration is established at all levels of organization, from minerals to formations inclusive. And if the dynamic subsystem, taking into account insignificant variations in the gravitational constant, has remained stable in the course of geological time, then the biogenic and geochemical subsystems have evolved irreversibly, which predetermined the overall irreversible evolution of landscapes and sedimentation situations.

The dynamic landscape subsystem is responsible for migration, differentiation, and formation of mainly terrigenous deposits. Considering the scale of terrigenous sedimentation, the role of dynamic processes is hard to overestimate. The regular reduction in energy levels in each of the facial hierarchies is primarily responsible for the organization of terrigenous masses. The transition from a high energy level to a lower one is the dialectic essence of the dynamic landscape's qualitative aspect. Hypsometric characteristics of the Earth's surface and its stepped-block structure determine the contrasting separation of characteristic links in the overall series of landscapes.

The continental step is represented by watershed spaces, the geomorphological scarps and slopes undercutting them, and, finally, accumulative plains. Each of them has its own sedimentological functions, consisting in mobilization of sedimentary material on watersheds, its appropriation and transit migration within the bounds of slopes, and accumulation on plains spaces. In this case, geomorphological scarps and slopes are the connecting link between the basic energy levels of the continental landscape, and their self-destruction in the course of its development determines their very high dynamic activity.

Analogous dynamic functions are carried out by marine and oceanic landscapes: underwater plains and the slopes and uplifts bounding them. In this case, the latter are also the most dynamically active; they perform enormous work on appropriation of the products of continental runoff, followed by delivery of them to the surface of underwater accumulative plains. The commonality of the problem of dynamic zonality in the piedmont step of dry land and the step separating a continent from oceanic and marine aquatories (underwater territories) is manifested in gravitational landslides, and the origin and development of turbidity flows, which form confluent or separate turbidite debris cones at the lower edge of the system's scarp. The more contrasting the gradation of the relief, the more clearly the landscape's zonality is manifested.

**In certain conditions, a large role may be played by a volcanogenic component (volcanoclastic or hydrothermal).

In the series of dynamic situations uniting continental, marine, and oceanic (basin) steps, a special position is occupied by boundary, coastal landscapes. They control the scale and means of continental-margin sedimentation, and also promote migration of sediments into remote parts of basins.

The principles of classification of landscapes according to dynamic traits were established in a discussion between V. V. Dokuchaev [3] and A. P. Pavlov [3]; the discussion continues to the present [6, 11-13, 18, 24].

A. P. Pavlov's supporters proceed primarily from analysis of the dynamics of processes of accumulation of genetic types of deposits. The effort to distinguish each genetic type, and especially groups and series of them according to the leading means of movement, without considering other processes, significantly reduces the effectiveness of the suggested classification. In nature, monodynamic processes are primarily manifested at the level of elementary landscapes. As they get larger, being superimposed one on another, they create a more complex picture, and the deposits formed within the bounds of such a landscape bear features of very complex polydynamics, i.e., they are, strictly speaking, polyfacial (polydynamic).

V. A. Dokuchaev's ideas about the polydynamic nature of landscape were developed by D. V. Nalivkin, V. I. Popov, Yu. A. Zhemchuzhnikov, P. P. Timofeev, and others in the classifications of facies that they worked out.

According to V. I. Popov [12, 13], the basic categories of landscape are polydynamic facial belts, each of which is characterized by a predominant process of sediment transportation peculiar to it, with which other, subordinate means of sediment transfer are connected. The process capable of transferring the whole mass of sediments from the beginning to the end of the independent dynamic facial landscape formed by them is classified as the leading one. Such interchanging belts include watershed-eluvial, slope, valley- and piedmont-fan, linear- and plains-valley, underwater-delta, bay-lagoon, coastal with different dynamics of the water environment, bottom-current, central-settling, and other facial belts. Each of them, possessing its own store of energy, realizes it in interconnected facial zones: of mobile clastic, moderately mobile pelitic, and conditionally stagnant, mainly chemo- and biogenic sediments. Each belt undercuts the preceding one. This zone of destruction and integration is the most important in appropriation of terrigenous material from the superjacent landscape; it begins the zonal differentiation of material of a new belt.

The classification worked out by Yu. A. Zhemchuzhnikov, P. P. Timofeev, and others also proceeds from ideas about the polydynamic nature of landscape, combining the leading and subordinate means of transportation of sedimentary material, individuated in the form of genetic types of sediments united by a single complex of facies.

According to these ideas, migration and deposition of sedimentary material are accomplished with the participation of different forms of movement of the water medium (temporary and permanent flows, currents, independent precipitation, etc.). In this case, for each facies (alluvium, delta, coastal shallow water, bays, lagoons, etc.) their combination is so specific that it enables us to talk about alluvial, delta, coastal shallow-water, bay-lagoon, and many other dynamic forms of migration and accumulation of sedimentary material. In this regard, each landscape is undoubtedly polydynamic.

Landscape is a dynamically mobile system tending, on the one hand, to differentiate and retain sedimentary material entering into it, and, on the other, to remove such material beyond its limits. According to the drop in energy potential, energy realization is expressed by individuation in the form of interchanging zones of accumulation of sediments of different particle-size classes, from the coarsest to pelitic. It is not by chance that the deposits of any facial belt are represented by a wide particle-size spectrum at various geomorphological levels of relief (on plains in landscapes near watersheds, coastal shallow water, continental-margin and remote parts of seas and oceans).

It would seem that such zonality would sharply reduce the possibilities for further delivery of clastic material to lower hypsometric steps of the relief and the emergence there of a new generation of zonally differentiated landscapes. Not enough attention has been given to resolution of these questions.

Along with processes of zonal differentiation, a unified system of transit flows is outlined: linear channels of mountain rivers, fan channels in alluvial fans, channels of plains rivers, breakthrough channels in deltas, rip currents in the wave-cut coast, underwater channels, "channels" in the composition of turbidity flows, and, finally, contour oceanic currents providing for global migration of terrigenous sediments from sources of clastic material all the way to the final runoff bodies of water. From the standpoint of balance, they are the most dynamically active. The transit properties of these flows are responsible for intensive migration of sedimentary material through the landscape, which is accomplished over the shortest distance at the maximum speed. For example, among such "subordinate" monodynamic facies we should mention fan channels dissecting alluvial fans, continuations of channels in the delta front, and also alongshore, rip, and runoff currents in the wave-cut belt. The volumes of these accumulations may occupy a modest place in the cross sections of sedimentary formations. However, it must be kept in mind that enormous masses of clastic material passed through

these channels, commensurable with the masses of terrigenous deposits accumulated at lower energy levels. The absence of such means of sediment transport in nature would sharply reduce the possibilities of migration of terrigenous components of different particle sizes from a superjacent facial belt to the next lower one. The question of the relationship of types of dynamics and distinguishing the leading means of movement among them is quite complex and can be resolved only by analyzing the actual volume ratios of genetic types of sediments and their genetic relations in specific cross sections of sedimentary formations.

The dynamic zonality of terrigenous sedimentation is strictly directed in each series of continental, coastal, and remote landscapes, which is expressed in contrasting individuation of the corresponding types of sediments of different particle-size classes. For example, in alluvium this is emphasized by the association of channel, floodplain, lacustrine, and bog facies; and within a piedmont alluvial fan, by the individuation of its clastic and pelitic parts, etc. However, in studying specific formations a more complex structure of paleolandscapes is revealed, and they themselves turn out to be richer in regard to types than follows from the suggested classifications of facies.

Piedmont molasse-forming landscapes can serve as an example. Their dynamic zonality is usually expressed in cyclic interstratification of coarse-clastic, aleuropelitic, and pelitic sediments with subordinate carbonate, sulfate, carbonaceous, and other accessory chemogenic and biogenic accumulations. In this case, the gradations of formations located closer to the source uplift are represented by coarse-clastic deposits; and remote ones, primarily by pelitic deposits. However, detailed study with the help of the facial method shows that their internal structure is more complex. Depending on peculiarities of orotectonics and paleogeography, and also paleoclimate, it is expressed in various facial combinations of alluvial-fan, alluvial—alluvial-fan, alluvial-fan—alluvial, and even just alluvial facies [1,10]. No less complex are the interrelations of piedmont molasse landscapes with the regions of denudation. In the conditions of ascending relief, linear valleys of mountain rivers, being embedded into erosion depressions, are separated from the head part of alluvial fans by a sharply expressed scarp of the relief. In the cross sections of such areas breaks occur. On the other hand, in the descending stage of the relief's development, when equilibrium of the river valleys' profile is established, their deposits find their continuation in accumulations of an alluvial fan or pass directly into deposits of plains alluvium.

The interrelations of conditions of piedmont sedimentation with the lower-lying landscapes of a longitudinal river replacing them turn out to be no less complex. Special forms of interrelation also arise depending on geochemical conditions and the landscape's biological productivity, when terrigenous molasse formations are carboniferous, red-bed, carbonate-containing, salt-bearing, etc. and may even be replaced by carbonate or evaporite formations. All of this is reflected in the structure of their cross sections.

The widespread practice of differentiation on the basis of the petrogenetic principle of series of formations (terrigenous, carbonate, halmeic, and silicite [13, 15, 22]), followed by separation of them according to the sedimentation situation is founded, in the end, on acceptance of the leading significance of processes of petrogenesis in a "pure form." In connection with this, should formations be understood as petrogenetically single-rock series of terrigenous, carbonate, halmeic, or evaporite deposits, or can they also be represented as more complex combinations of petrogenetic types: terrigenous-carbonate, carbonate-halmeic, pelitosilicite, and many others? The latter seems more correct to us, if we recognize that such combinations are genetically determined by the unity of sedimentation and formation-developing situations. Otherwise, it would be very hard to draw a boundary between sediments and the formations created by them.

This principle is also valid for studying and classifying genetic and facial types of sediments the component composition of which reflects the joint influence of terrigenous, biogenic, chemogenic, and sometimes volcanogenic sedimentation — the three basic landscape subsystems. Being most clearly displayed at the level of organization of sedimentary material, in an integrated form they also predetermine the general course of formation development. For example, accumulation of terrigenous sediments and creation of their structure are primarily determined by dynamic processes, while their specialization with respect to certain types of sedimentary mineral resources and authigenic accessories reflects the special role of geochemical and biochemical processes. On the other hand, development of carbonate, halmeic, and silicite sediments (formations) is predetermined not only by the kinematic properties of landscapes, but also by their biological productivity and geochemical characteristics.

In V. I. Popov's opinion [10, 12], chemogenic and biogenic processes are subordinate to dynamic processes. The scale and rate of their development grow as the energy drops in each facial belt, and their manifestations are maximum in remote parts completing its zonality, i.e., in the conditionally stagnant zone. However, such an understanding of the role of biogenic and geochemical processes and subordination of them to the dynamic factor make it hard to explain the development of primarily carbonate, halmeic, and evaporite formations, complex combinations of terrigenous sediments

with biogenic and chemogenic ones, specialization of formations for various mineral resources, etc. Genetic types of sediments, and their associations and facies, including formations, like the processes that give rise to them, cannot exist and develop apart from their relationship with each other. For example, the transition of terrigenous molasse and coastal (schlieren) complexes to carbonate or halmeic ones indicates basic changes in the conditions of their accumulation; dynamic processes become subordinate and are replaced by bio- and chemogenic ones.

Variability of the situations of geo- and biochemical landscape subsystems is due to the extreme diversity of the forms of migration of chemical elements. Various mechanisms of their functioning (photosynthesis, biofiltration, chemical precipitation, coagulation of colloids, etc.) react very sensitively to changes in suprasystem factors (tectonic conditions, climatic conditions, sources of material, etc.). In contrast to dynamic situations, which are determined by the gravitational constant, they evolve irreversibly in the course of geological time. It is not by chance that the study of processes of the evolution of landscapes and their unrepeatability in the Earth's history are based primarily on reconstructions of bio- and geochemical landscape subsystems.

Migration and accumulation of chemical elements and their compounds occur under the direct or indirect influence of living matter and products of its transformation. The geochemical situation of landscapes, with rare exceptions, is created under the influence of the biosphere. In essence, biogenic and geochemical processes are so interrelated that at times it is hard to separate them. According to V. I. Vernadskii [1], these are biogeochemical processes.

Classifications of biogeochemical facies*** were developed by L. V. Pustovalov [14], N. M. Strakhov [16], A. I. Perel'man [9, 10], and others. They are based on study of biological productivity, acid-alkaline and oxidation-reduction characteristics of the landscape, and also the number and composition of chemical elements participating in migration. The migration barriers arising in this case should be seen as basic links of the biogenic and geochemical landscape subsystems that we have distinguished; their development is governed by the laws of facial zonality. They are organized by levels and evolve irreversibly in time.

Probably the largest categories of these subsystems correspond to the types of continental, oceanic, and volcanogenic-sedimentary lithogenesis**** outlined by N. M. Strakhov. Their number should be enlarged on account of situations that have disappeared in the course of development of the Earth's crust and therefore have not been repeated in later epochs [28]. Specialization with respect to the type of sedimentogenesis implies such manifestation of bio- and geochemical processes, when they unite a single series of associated facial landscapes of a whole sedimentation basin or a large part of one. They can be distinguished and typified with the use of principles suggested for the dynamic subsystem, when the means of differentiation and accumulation of chemical elements, and facial bio- and chemical relations are taken into account from the standpoint of the balance of matter. They are organized by level, which agrees with the hierarchy of structural-material systems — from genetic types of sediments to formations inclusive. At the level of elementary landscapes, biochemical situations are quite variegated and combine different relationships of oxidation-reduction and acid-alkaline conditions, different biological productivity, etc.

For example, the typical landscapes of arid sedimentogenesis are characterized by low biological productivity, and by a shift of geochemical conditions in the direction of overall alkalinity and oxidation, with increased values of evaporative concentration. As a result, sedimentary accumulation is red-bed and carbonate-containing. These traits are the leading ones — they permeate the whole landscape. A change in alkalinity and evaporative concentration laterally is expressed here by individuation of a number of more fractional interchanging landscapes forming a regularly structured facial series of sedimentary accumulations, all the way to halmeic eutonic. Reacting sensitively to external conditions, red-bed carbonate sedimentation is specialized with respect to processes, as well as their mineral reflection (minerals with a high degree of oxidation, increased contents of carbonate, gypsum, copper, etc.). Superposition of reduction processes on this overall zonality makes more fractional regionalization possible.

Humid landscapes, with their high biological productivity, are distinguished by predominance of acid situations with areas of reduction superimposed on them. These situations determine the migration and accumulation of hard-to-dissolve chemical elements, and also of elements with variable valence.

***The authors believe that isolation of biogeochemical and other such "facies" is invalid, since these are only aspects of ordinary sedimentological facies.

****In our understanding, these are types of sedimentogenesis.

The special role of the biochemical factor is most fully manifested in carboniferous formations. The main peculiarity of their development, polygenesis, is due to different sources of sedimentary material (peats and the terrigenous sediments surrounding them) and to various mechanisms of its differentiation and accumulation. According to dynamic ideas, peat bogs occupy peripheral, dynamically less active zones of landscapes. They primarily include lowland coasts of ancient marine bodies of water that had a large extent (the coastal type of ancient peat accumulation), and small thickness (no more than 1-2 m, for the most part) of coal seams. The Donets, Ruhr, Illinois, a number of English coal basins, etc. are characteristic mainly of the Paleozoic. The Mesozoic, Cenozoic, and modern epochs are characterized by the delta (river mouth) and valley-river types of peat accumulation: large thickness (as much as 50-100 m, sometimes more) of coal seams. Coal seams of these types practically all change to a fossil state and make up all of the contemporary coal basins and deposits. Besides that, they can become boggy and form thin interlayers and lenses of peat, alluvial fans, floodplains, overgrown lakes and lagoons, depressed spaces of large lowlands, and other areas of the ground surface, but, with few exceptions, they practically do not change to a fossil state and have no practical significance [18].

Carboniferous formations differ from coalless ones primarily in the high, almost explosive biological productivity of the landscapes that give rise to them. In the direct sense, the latter were characterized by expansion of the biosphere, when processes of terrigenous sedimentation were practically completely overwhelmed, giving way to accumulation of photosynthesis products. Watershed and slope peat bogs, in this case, ran together with lacustrine-bog, plains and lowland, maritime ones, forming an enormous continuous cover. Their position is analogous to limestone horizons in paralic carboniferous strata, where accumulation of peat bogs and carbonates was predetermined by the landscape's high biological productivity with minimal sediment runoff.

The situations of peat accumulation are landscapes with sharply limited and localized sediment runoff. The combination of intensive terrigenous sedimentation with explosive accumulation of organic matter in peat bogs is the main specific feature of development of carboniferous (peat-bearing) formations. In this respect, they have no analog among the multitude of terrigenous formations.

The biogenic and geochemical landscape subsystems react very sensitively to the slightest change in paleoclimate or tectonic conditions, which leads to a rapid change in types of sedimentation. This explains the individuation of various formations in cross sections of the Earth's crust, their cyclic stratification with a set of authigenic minerals and mineral resources characteristic of each section, the separation in time of epochs of salt and copper accumulation, bauxite and peat accumulation, etc. In each such epoch, lateral series of formations, like the formations themselves, are specialized with respect to biogeochemical processes, as well as their structural-material reflection.

One of the critical problems of modern lithology is comparative historical-geological analysis of processes of sedimentation (sedimentogenesis) expressed in regularly structured evolutionary series of sedimentary formations. Like all other geological categories, they have evolved irreversibly in the course of geological time. Formations of the same type from each of the epochs are individual and differ from earlier and later ones in a number of peculiarities characteristic of them alone.

These aspects of nascent formation analysis, like the teaching as a whole, began to develop comparatively recently. Getting to know the general features of different-aged formations of the same type will undoubtedly be the most important task of formation investigations. However, only comparative analysis of them, and isolation and study, first of all, of the differences between formations of the same type will open new possibilities in acquiring knowledge of their genesis and developing a better classification of them.

In connection with the need for deeper study of the facial and formation zonality of sedimentation basins, and for clarification of peculiarities of their development and irreversible evolution, there is an urgent need for further improvement of methods of facial analysis and typification of the sediment-accumulation landscapes of sedimentation basins and systems of them. In turn, since formation analysis should be, in essence, a continuation of facial analysis and a higher level of organization of knowledge primarily of the sedimentary process, it is necessary to organize appropriate research. N. S. Shatskii [25] laid the foundations of formation analysis as a new direction in geology back in 1939 and devoted practically his whole scientific activity to seeking ways of creating a unified teaching about geological sedimentary formations, which must be based, first of all, on the fundamental divisions of geological sciences. And most important was his conclusion as an ideologist of formation analysis, to which he came by the end of his life, i.e., in 1960. "I clearly see," he wrote, "that all of this is only the beginning of research in this field, but it seems to me that study of sedimentary-volcanogenic (and, undoubtedly, sedimentary – P.T.) parageneses in the future will go in precisely this direction, along the path of revealing the genetic relationships between rocks" [27, p. 172].

The systems approach must include obligatory study of genetic and facial types of sediments, with consideration of the absolute masses of sedimentary material. It will expand and deepen genetic ideas, open up new possibilities for development of a comprehensive procedure of formation analysis, and lead to creation of better classifications of facies and formations, based primarily on peculiarities of their internal structure, the composition and the origin of sedimentary deposits, and regionalization and typification of the sedimentation basins containing them. In essence, we are present at the creation of a new direction in geology: comprehensive facial and formation analysis as the basis for systems analysis of a new level of organization of investigations of sedimentary deposits, i.e., a teaching about geological sedimentary and volcanogenic-sedimentary formations.

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GENETIC GROUPS OF ORE-BEARING EXOGENOUS FORMATIONS

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UDC 551.7.022:522.1

Three genetic groups of ore-bearing exogenous formations are distinguished: hypergene, sedimentogenic, and epigene. Their typification is based on the time and means of formation of ore concentrations, and also their position in the structure of sedimentary-rock basins. The question of the role of paleohydrogeological factors in epigene redistribution of ore material is considered.

Discrimination, systemization, and mapping of ore-bearing geological formations is one of the most important and, at the same time, insufficiently studied problems of regional minerogenic analysis [10, 12-14, 16, 17]. Terms and concepts relating to ore-bearing geological formations are presently used rather widely in the literature devoted to regional minerogeny (metallogeny). In this case, the definition given by D. V. Rundkvist is, in essence, generally accepted (and adopted in the present article): "an ore-bearing formation is a geological formation possessing a specific composition and structure, with which deposits of mineral resources are genetically or paragenetically connected in space and time" [10, p. 16]. It is only necessary to note that an ore-bearing formation is not only a geological, but also a geological-economic concept. A change in the conditions for a deposit of mineral resources connected with economic factors can cause a geological ore-bearing formation to become nonore, or vice versa.

In the domestic literature, ore-bearing formations are subdivided according to various traits into parent, productive, typomorphic ones, etc. At the same time, questions of genetic classification of these formations and, in particular, of ore-bearing exogenous formations have not yet been covered in the literature.

Analysis of the data in [2, 3, 5, 8, 10, etc.] shows that ore-bearing exogenous formations can be subdivided according to the conditions of formation of deposits of mineral resource confined to them into three basic genetic groups: hypergene, sedimentogenic, and epigene.

The hypergene group includes ore-bearing exogenous formations with deposits originating in the zone of hypergenesis in the process of concentration of ore elements (compounds) at various types of hypergene barriers (mechanical, physicochemical, biological). The barriers are located either directly at the ground surface (surface hypergenesis), or inside the zone of hypergenesis at depths of tens or many hundreds of meters (subsurface hypergenesis), including interbed infiltration artesian systems (often with uranium and other mineralization), zones of subsurface hydrolysis, etc. [5, 11, 18, etc.].

In general terms, the minerogeny of a specific zone of hypergenesis is determined by climate, the layout of the relief, and the regional geological structure existing at the time of the zone's formation. All of these factors were intensively modified in time. Analysis of the evolution of formation of hypergene ore makes it possible to distinguish in the geological history of the territory of the former USSR a number of ore-bearing epochs of formation of hypergene ore, to which the origin of practically all of the hypergene ore-bearing formations are confined (Fig. 1).

Commercial ore-bearing hypergene formations (containing balance ore reserves) in the territory of the former USSR are only known beginning from the Middle Devonian. And this is to be expected, for only since the Middle Paleozoic (at least in the territory of Eurasia), as a result of the planet's evolutionary development, did vegetation appear and conditions arise that were favorable for formation of thick, chemically differentiated weathering crusts [6].

The following epochs of hypergene ore formation are clearly established: D₂-D₃, C₁, T₃, K, and P₃. Each of the epochs is characterized by a range of occurrence and peculiarities of minerogeny.

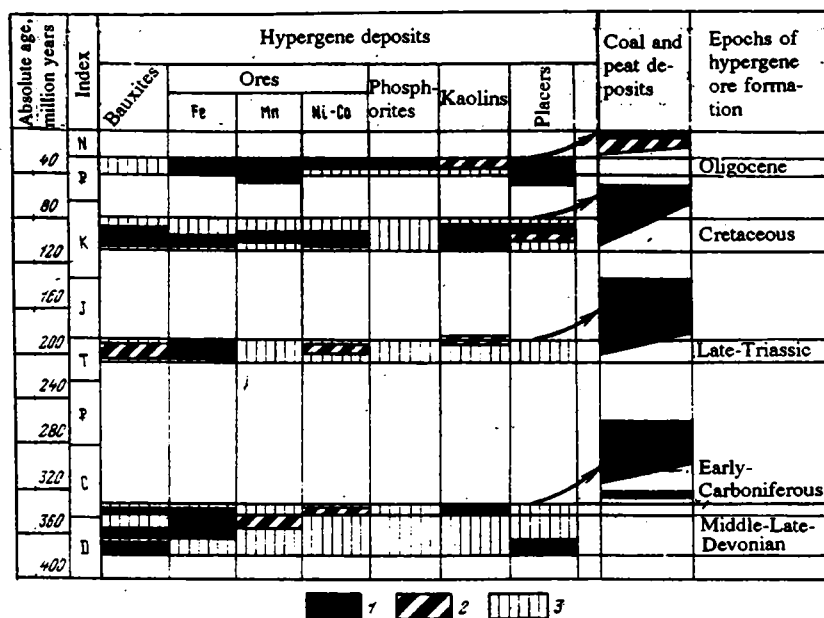


Fig. 1. Diagram of distribution of hypergene deposits in the geological cross section of Devonian–Quaternary sedimentary rocks in the territory of the CIS: 1) commercial deposits; 2) noncommercial deposits, ore manifestations; 3) epochs of hypergene ore formation.

The Middle-Late-Devonian epoch was manifested in limited areas (the Urals, Timan, Northern Kazakhstan, central regions of the Russian platform). The epoch is characterized by formation of bauxite- and iron-bearing deposits, rare-metal and phosphorite ores in weathering crusts, and titanium placers transported from nearby sources.

Commercial ore-bearing hypergene formations of the Early-Carboniferous epoch, which contain bauxites, rich iron ores, and refractory materials, are localized exclusively within the bounds of the Eastern European craton.

It is fundamentally important to note that both Paleozoic epochs of hypergene ore formation were manifested only in the western part of the former USSR (as far as the Urals and Northern Kazakhstan inclusive). There is still no definitive explanation for this phenomenon. The most likely is the hypothesis that, at that time, the Siberian craton was a considerable distance away from the Eastern European one and located in different (unfavorable) climatic situations [6].

The range of occurrence and ore content of deposits of the next (Late-Triassic) epoch is limited to the Hercynides of the Ural–Tian-Shan region. The minerogeny of this epoch is diverse. In the Late Triassic, on the edges of coal-bearing depressions of the Urals and Central Asia, probably confined to rift zones, ore manifestations of bauxites, iron deposits, and ore manifestations of nickel within the bounds of ultrabasic masses occurred. The development of a hypergene gold-hematite-calcite formation in Central Asia is dated in the Late Triassic.

The most productive for the whole territory is the Cretaceous epoch of hypergene ore formation (or rather, the Aptian-Turonian one). Cretaceous weathering crusts and products of their nearby redeposition are known practically from Ukraine in the west to the Khankai mass in the Far East, and from Southern Tian Shan to the border of the Anabar mass inside the Arctic Circle. We have to suppose that in the middle of the Cretaceous period a global unification of the Earth's temperature and water conditions occurred, probably due to external (cosmic) factors.

In the Cretaceous epoch of formation of hypergene ore, along with bauxite-bearing formations, nickel-bearing, phosphorite-bearing, kaolin-bearing, rare-metal, and gold-bearing formations originated, as well as eluvial placers of titanium and tin minerals, numerous ore caps (manganese, iron, gold-containing, and polymetallic), and also a large complex of karst ore-bearing formations [4, 6]. Analysis of the map of exogenous minerogeny of the USSR [3] makes it possible to establish a definite zonality in the distribution of hypergene formations of the Cretaceous. The maximum of commercial hypergene ore formation is observed within the bounds of a broad band stretching from southern regions of the European part of the former USSR through the Urals and the northern half of Kazakhstan to Salair and on to the Enisei chain of hills. To the north, east, and south of this band, the ore content of hypergene formations is sharply reduced or characterized by different minerogenic specialization. In particular, in the southern part of Kazakhstan and in the mountain

ranges of Central Asia beyond the Aral rampart bauxite-bearing formations of the Cretaceous level are facially replaced by siliceous, variegated, carbonate one with horizons of arid caliches with rare-metal mineralization.

In the north, bauxite content of the Cretaceous level is noted at high latitudes (beyond 60° north latitude), but the ore deposits developed there, as a rule, are made up of lean ores. Kaolinite in the composition of sedimentary rocks is gradually replaced by minerals of the hydromica and montmorillonite groups, which indicates relatively weak differentiation of material occurring against a background of intensive hydrolysis. Such situations are favorable for the development of iron- and nickel-bearing, eluvial-placer formations, which is noted in high-latitude regions with favorable geological structure, in particular, in the Northern and Arctic Urals, and in the northern part of the Siberian craton.

A special place in formation of hypogene ore is occupied by its last (Late—Cenozoic, or rather, Oligocene—Quaternary) stage and the Oligocene epoch of ore formation confined to it. At that time, the territory under consideration left the zone of hot, humid climates most favorable for development of thick, large-area weathering crusts that are chemically transformed to a significant degree. Therefore, there are no extensive laterite covers here, which are characteristic of the Earth's contemporary tropical zone [5].

Hypergenesis of the Late Cenozoic in the territory of the former USSR is characterized by considerably different characteristics, due not only (and, in a number of cases, not so much) to climatic as to tectonic factors. Intensive block movements with amplitudes sometimes reaching several kilometers (for example, in the Tian-Shan mountains) occurred in various regions here during the whole second half of the Cenozoic. This circumstance created thick crushing zones, altering the direction and rate of movement of groundwaters. The Oligocene—Quaternary is more characterized by linear zones of subsurface hydrolysis and deep karst depressions (sinkholes, funnels, caves, etc.). The ore content of these geological structures was formed on account of surface water, as well as plutonic solutions ascending through weakened zones. Regions of Late-Cenozoic activation are particularly characterized by thick zones of oxidation of sulfide ores, sometimes reaching hundreds of meters. Processes of oxidation, hydration, and hydrolysis took place (and continue to take place) intensively not only in a humid climate, but also in arid zones (for example, in Central Asia), and also in permafrost conditions (cryolithogenesis). In analyzing the map of exogenous minerogeny of the USSR [3], synchronicity of the establishment of a number of hypogene ore-bearing formations and epochs of magmatic (volcanic) activity and tectonic activation is clearly confirmed (for example, the Triassic of the Siberian craton, the Cretaceous of Tian Shan, the Middle Devonian of the east slope of the Urals, etc.). Epochs of commercial coal accumulation usually follow immediately after epochs of formation of hypogene ore, completing the continental (pretransgressive) stage of the region's development (see Fig. 1).

The sedimentation group is the most extensive and diverse in types of deposits of mineral resources. The ore material in formations of this type was accumulated in the stage of sedimentogenesis and did not undergo any significant displacements in the stages of diagenesis or catagenesis (late diagenesis).

Sedimentogenic formations are subdivided into three subgroups: sedimentation, sedimentation-diagenetic, and sedimentation-dia-catagenetic.

In ore-bearing formations of the *sedimentation subgroup*, deposits originated in the stage of sedimentation (various placers, deposits of sand, gravel, etc.). In connection with this, their genesis, composition, and structure are determined, to a significant extent, by paleogeographic features of the region.

Thus, for example, placers transported from nearby and remote sources are distinguished, regardless of the useful component (metal).

The formation of nearby placers (gully-draw, ravine, etc.) practically does not depend on the climatic sedimentation situations, but is determined by the dimensions of ore concentrations in the primary sources, the duration and nature of their transportation, and geomorphological conditions. In connection with this, nearby placers developed throughout the time of the continents' geological development. Forming in denudation regions, these placers are readily subjected to destruction and therefore are presently found, for the most part, only among Neogene—Quaternary deposits.

For remote placers, a direct genetic link with epochs of formation of hypogene ore is established. Among placers of this type, the most common are coastal-basin zircon-rutile-ilmenite ones formed by means of prolonged active hydrodynamic sorting of redeposition products of clay weathering crusts. In the regional distribution of remote placers, they are definitely confined to the slopes of shields and paleouplifts of ancient and epipaleozoic cratons. In particular, the most productive Paleogene zircon—rutile—ilmenite placers, sometimes containing monazite, diamonds, and other minerals resistant to weathering, border the west and east slopes of Mugodzhari; in the form of a broad band, they stretch along the

east slope of the Southern Urals; and on the north they border the Kazakhstan shield, Salair, and the Tom-Kolyvan folded region.

Ore-bearing formations of the *sedimentation-diagenetic subgroup* are characterized by formation of ore bodies in the stage of diagenesis, mainly by means of concentric segregation of sedimentation ore material around various types of centers (concretion pisolitic, oolitic, and spherulitic ores). In this case, depending on the pH-Eh of conditions of the diagenetic environment, specific mineral types of ores occur. For example, chamosite or hydrogoethite iron ores, rhodochrosite or vernadite-psilomelane manganese ores, etc.

The same subgroup includes formations with salt deposits, the crystallization of which occurs in the stage of diagenesis (native lake salt, etc.), and also peat deposits undergoing humification.

The *sedimentation-diacatagenetic subgroup* combines ore-bearing formations the deposits of which were formed in the stage of catagenesis from ore material that had undergone usually diagenetic transformations. This group includes some formations with iron-ore deposits transformed in the catagenesis stage (for example, red iron ores), ancient cemented placers, brown and black coals, and deposits of rock and potassium salts.

Epigene Group. Epigene ore formations are characterized by introduction of ore components into already formed sedimentary strata undergoing catagenesis. Deposits of the epigene group of ore-bearing formations originate in the process of prolonged evolution of sedimentary (and volcanogenic—sedimentary) basins by means of extraction of ore components from the rocks by groundwaters (mostly sedimentogenic and ancient-infiltration, and also rejuvenated), followed by selective concentration of them at various ore barriers [1, 7, 8, 18].

Creation of epigenic ore-bearing formations (copper-bearing, lead-zinc, oil- and gas-bearing, etc.) in sedimentary basins is mainly connected with elision (exfiltration) migration of sedimentogenic, ancient-infiltration, and catagenic (rejuvenated) groundwaters. Elision water-pressure systems in the zone of catagenesis are created as a result of various processes (compaction, recrystallization of rocks, etc.) leading to migration of groundwaters to the surface. In this case, in elision systems groundwaters move mainly upward through the cross section through fault zones and other zones of increased permeability, and also through highly permeable beds from central parts of a basin to its margins. These processes are significantly activated by rearrangement of the structural plan of sedimentary basins and by changes in their geotectonic conditions.

For the most part, groundwaters in the zone of catagenesis have a chloride composition, with mineralization from 20 to 350 g/kg, often inherited from the waters of the sedimentation basin. Processes of gas formation (CH_4 , less often H_2S or CO_2), which are mostly connected with decomposition of organic matter and reduction of sulfates, have a large influence on the dynamics and composition of groundwaters in the zone of catagenesis. In the zone of catagenesis, groundwaters interact with rocks enriched with various metals (Pb, Zn, Cu, Fe, Mn, etc.). During inversions and structural rearrangements, especially those accompanied by magmatic activity, migration of groundwaters in the zone of catagenesis is significantly stimulated. In this case, displacement and interaction of the waters of previously isolated water-pressure complexes occur in fault zones, leading to formation of geochemical barriers at which ore deposits develop.

Creation of ore deposits in the zone of catagenesis can be accomplished according to different genetic models. Thus, for example, in some cases sulfide ore deposits are formed as a result of interaction of metalliferous chloride brines with hydrogen-sulfide-containing groundwaters in fault zones. Such genesis is most likely, for example, for the Dzhezkazgan copper-ore deposit.

Processes of ore formation are fairly widely realized in the zone of catagenesis of sedimentary basins in connection with decomposition of complexes of the type $\text{MeS} \cdot n\text{H}_2\text{S}$ in hydrogen-sulfide-containing chloride brines when they migrate along a seam pitch from deeply buried parts of basins to peripheral parts: the Rovno-Dnestr, copper-polymetallic with fluorite, structural-metallogenic zone ($V_2 - \text{C}$), and the Gaurdak-Kugitan, lead—zinc, sulfur-bearing zone (J etc.). It is important to note that processes of epigenic ore formation (sulfide ores, fluorite, etc.) are often clearly associated with the formation and migration of oil and gas reservoirs.

Magmatic activity in the zone of catagenesis of sedimentary basins leads to a sharp rise in temperatures, chemical activity, and processes of groundwater migration. In turn, all of this results in a sharp intensification of processes of redistribution of metals and removal of them from cooling magmatic bodies intruded into the sedimentary mantle. In equal conditions, sedimentary basins possess higher potential ore content in the zone of catagenesis with a predominance of strong (270-350 g/kg) chloride calcium-sodium (and calcium) metalliferous brines, which are genetically connected with halmeic formations. Hydrogeochemical and paleohydrogeological analyses of a number of structural-metallogenic zones

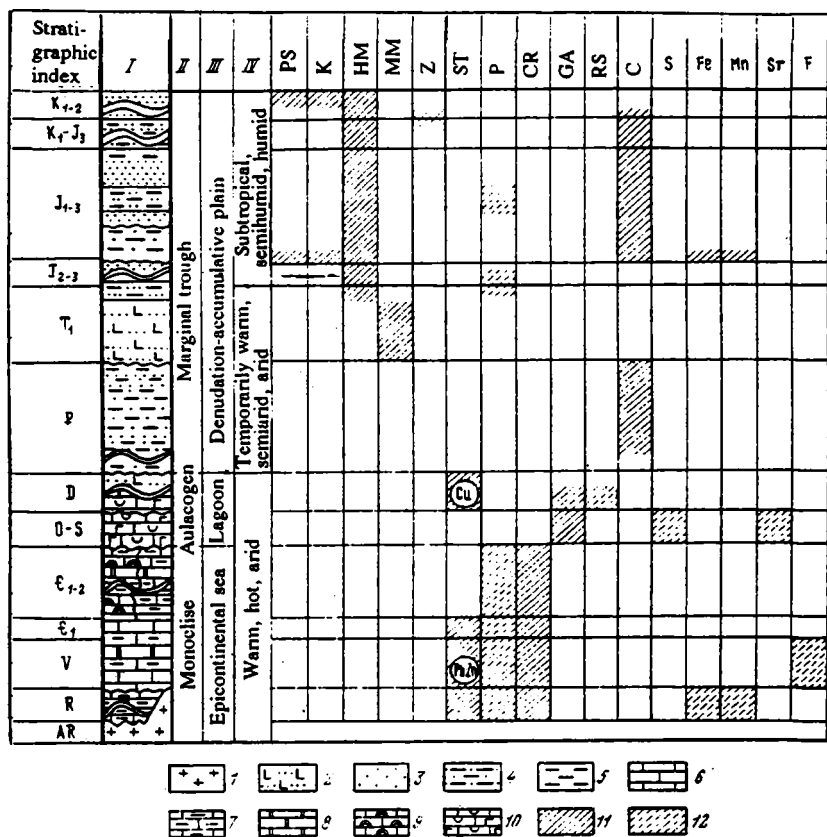


Fig. 2. Schematic prototype of a basinogram: I) lithological cross section; II) tectonic structures; III) elements of paleogeography; IV) climate; 1) basement formations not subdivided by composition; 2-10) the basin's deposits (2 - volcanogenic, 3 - sandy, 4 - sandy-clay, 5 - clay, 6 - limestone, 7 - limestone-clay, 8 - dolomite, 9 - reefogenic-limestone, 10 - sulfate-halmeic-limestone); 11-12) position of ore-bearing exogenous formations with proven and supposed ore content, respectively. Types of mineral resources: QS - quartz sands, K - sedimentary kaolin, HM - placers of heavy metals, MM - bentonite clay, Z - zeolite rock, ST - stratiform deposits, P - phosphorite, CR - carbonate rocks, GA - gypsum-anhydrite, RS - rock salt, C - coal, S - native sulfur, Fe - iron, Mn - manganese, Sr - celestine, F - fluorite.

of sedimentary basins in the territory of the CIS with respect to stratiform lead-zinc (often with fluorite) mineralization (in particular, Rovno-Dnestr, Dubno-Gorodok, Starobel'sk-Millerov, Gaurdak-Kugitan, Borislav-Pokut, etc.) everywhere shows their interrelation with underground, exogenous (mostly sedimentogenic), chloride brines. We should especially emphasize that stratiform lead-zinc (often with fluorite) mineralization in sedimentary basins with exogenous chloride brines occurs in these basins regardless of manifestations of magmatism.

The epigene group of ore-bearing formations is characterized by their frequent confinement to marginal parts of basins associated with long-lived fault systems, which is connected with the migration of ore-bearing solutions from internal buried parts of the basins upward along seam pitches and fault zones and is important in prediction.

Special study of ore-bearing exogenous formations, including their genetic aspect, was performed during compilation of the "Map of exogenous minerogeny of the USSR on a scale of 1:5,000,000" [3], and also in preparation of a number of methodological guides to the principles and methods of estimating the ore content of geological formations [2, 5, 9, 10]. In doing so, it was shown that ore-bearing exogenous formations are mostly confined to various types of sedimentary-rock basins. The latter are a set of paragenetically related sedimentary (and volcanogenic-sedimentary) formations regularly confined to negative structures of the Earth's crust existing for a long time.

In the process of the basin's development, the sedimentary (and volcanogenic-sedimentary) formations composing it undergo diverse postsedimentation changes as a result of the energetic activity of groundwaters, usually accompanied by formation and, in a number of cases, reformation of deposits created previously. Thus, the same geological formation may

belong to different ore-bearing formations in different stages of the basin's development, or it may change from ore-bearing to the category of nonore formations. It is also important to note that the study of exogenous minerogeny and discrimination of ore-bearing formations in sedimentary-rock basins must be carried out with obligatory analysis of their hydrogeological (paleohydrogeological) conditions. Sedimentary-rock basins are usually fairly autonomous hydrogeological structures of the artesian- and adartesian-basin type, which are characterized by a certain direction of ore-forming processes, depending on the structure of the formations composing them and manifestations of tectonomagmatic activation [1, 2, 15]. It should be noted that the history of formation and peculiarities of minerogeny of individual sedimentary-rock basins are quite distinctive. This circumstance makes it very hard (and, in a number of cases, completely impossible) to create generalized predictive models. For predictive evaluation, it seems to us more promising to study in detail the characteristics of each basin's geological structure, and to compose basinograms (Fig. 2) and reference paleohydrogeological columns [15].

Analysis of data obtained in the process of such investigations makes it possible to estimate most fully and economically the prospects of basins for discovery of exogenous deposits in them.

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Analysis of data on exogenous minerogeny makes it possible to substantiate the discrimination of three main genetic groups of exogenous ore-bearing formations and deposits associated with them: hypergene, sedimentogenic, and epigene. The formations and deposits of each group are characterized by strictly individual patterns of development and, accordingly, predictive criteria for prospecting for mineral resources.

It is suggested that construction of predictive prospecting complexes for hypergene deposits be based on the clearly expressed pattern of their confinement to the epochs of hypergene ore formation that have been revealed. All of the known commercial hypergene deposits in the territory under consideration originated in these relatively brief segments of the Earth's geological history.

The bases for constructing predictive prospecting complexes for sedimentogenic ore-bearing formations should be discrimination and detailed study of the history of development of specific sedimentary-rock basins as sets of paragenetically interrelated sedimentary and volcanogenic-sedimentary formations confined to negative structures of the Earth's crust that existed for a long time.

The patterns of localization of epigene ore-bearing formations and deposits, which are also confined to sedimentary-rock basins, are determined, to a significant extent, by paleohydrogeological factors, the evolution of magmatism, and the nature of tectonic movements.

Magmatic activity (and the hydrothermal activity usually accompanying it) has a significant effect on formation of deposits of all of the genetic groups, usually intensifying the process of ore formation and involving a broader spectrum of useful components in it. In this case, a number of ore elements, gold, tungsten, and molybdenum in particular, practically do not form primary deposits without an "endogenous stimulus" in exogenesis [5].

Each genetic group of ore-bearing formations and deposits is characterized by strictly individual patterns of formation of ore bodies, and also by age intervals of their most widespread occurrence (ore-bearing epochs) and therefore requires development of a set of predictive criteria characteristic of it alone.

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GEOCHEMICAL PATTERNS OF FORMATION OF MINERALS OF THE COARSE FRACTION OF SOILS OF ASSOCIATED LANDSCAPES OF CENTRAL CISCAUCASIA

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UDC 550.4:551.234(470.6)

Based upon data from optical microscopy, x-ray diffraction, and IR-spectroscopy, we have classified and described groups of clastogenic igneous and metamorphic minerals, minerals of chemical-sedimentary origin, and authigenic minerals and formations formed in soil as a result of pedogenesis and recent geochemical processes. An analysis of the distribution of minerals of various origins in the soils reveals the role of geochemical interlinking of the landscapes in the formation of the mineral mass in the chernozems, and alluvial zones of the steppe zone.

The mineral composition of soils in the steppe zone is primarily formed by material from soil-forming rock and by soil-geochemical processes which transform the original substrate to one degree or another. A combination of processes are responsible for the original composition of soil-forming deposits as well as the direction and degree of transformation of such deposits during soil-formation. These include mechanical processes, physicochemical processes, biogenic and technogenic migration [19], and also a combination of processes which transform material during migration to the site. The geochemical structure of the landscape [8], reflected in the structure and properties of the soil cover, is formed as a result of the action of these processes [23]. However, the geochemical makeup of the landscape has been studied primarily in terms of chemical elements and fairly simple chemical compounds. Less attention has been devoted to the complex substances and species of chemical compounds actually participating in natural soil-geochemical processes. Minerals in the coarse fraction of soils include a broad range of such species. They play an important identificational role in the study of processes associated with migration of mineral material and, especially importantly, processes of transformation of the original substrate and mineral formation during pedogenesis.

For this reason, the goal of the present investigation was to identify and analyze the distribution of terrigenous and authigenic (pedogenic) material in soils of adjacent landscapes in Central Ciscaucasia in order to discover the source areas of such material and to clarify processes of later redistribution within the landscape as well as transformation of the original substrate and mineral formation at the site during pedogenesis.

Existing regional investigations of this question mainly cover the mineral compositions of Quaternary loessal deposits distributed over the plain adjacent to the Stavropol' uplands [1, 2, 4, 6, 7, 15, 26, 27]. The loessal cover, according to data from these investigations, has no direct relation to the deposits underlying it and exhibits areal homogeneity and persistence of mineral composition. The heavy fraction of the cover contains amphibole, mica, (frequently) pyroxene, and also magnetite, ilmenite, zircon, rutile, chlorite, apatite, granite, and tourmaline; it contains almost no metamorphic minerals.

The data on the mineralogy of the soil-forming rocks of the Stavropol' uplands (the Maikopian and Sarmatian deposits) is less extensive. Zatenatskaya [11] found large quantities of iron oxides and hydrous iron oxides (limonite, goethite, and magnetite), ore minerals, pyrite, hornblende, pyroxenes, epidote, granite, zircon, and carbonate in the composition of the heavy fraction of Maikopian deposits. In addition, disthene, staurolite, muscovite, biotite, sphene, apatite, chlorite, rutile, and leucosene were discovered in weathered varieties of these deposits.

In the mineralogy of the soil-forming rocks of different ages, there are both similarities, most pronounced in the composition of clastogene minerals, and differences, reflected in the composition of authigenic minerals, which formed as chemogenic-sedimentary minerals in one case in a marine paleobasin and in a subareal environment in another case.

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TABLE 1. Characteristics of Natural Conditions and Soils of Macrocatenas

Soil	Topograph- ical setting	Absolute altitude	Humidity factor	Soil-form- ing rock	Thickness of humus horizon, cm	Content of C _{org} in 0-25 cm layer, %	Average content of frac- tions along profile, mm		Depth of blistering from HCl, cm	Groundwater level, m; fluctuation in m)
							<0,001	<0,01		
Mesocatena 1										
Typical chernozem	Water divide surface	540	0,9	Eluvial clay	110	3,1	35,4	57,8	55	>10
	Floodplain	420	0,9	"	88	1,9	31,7	40,7	From surface	0,6 (0,5—1,5)
Mesocatena 1										
Common chernozem	Water divide surface	440	0,8	Eluvial- deluvial clay	95	2,8	37,8	49,8	"	>10
Mesocatena 3										
Same	Same	320	0,5—0,7	Loesslike loam	104	2,0	23,6	38,7	"	>10
Mesocatena 4										
Dark chestnut	Flood- plain- meadow	200	0,4—0,5	Loesslike loam	44	1,2	24,3	38,1	From surface	>10
Flood- plain- meadow	Floodplain	170	"	—	—	2,2	26,3	41,5	"	0,5

The latest association of authigenic minerals and formations reflecting the behavior of the landscape as a whole in its contemporary form were probably created as a result of landscape-geochemical and soil processes taking place in a system of adjacent landscapes.

Objects and Methods of Investigation. Soils of geochemically adjacent landscapes composing a macrocatena on the eastern slope of the Stavropol' uplands served as the object of investigation. The length of the macrocatena extending from the Prikalaussk Heights to the Otkaznensk reservoir, is ≈ 100 km. In the vicinity of the Prikalaussk Heights and at distances of 17, 39, and 100 km further to the south-east, we selected four mesocatenas; in each of these, sections for soil examination could be located by geomorphological relief forms (water divide, slope, floodplain). These mesocatenas, as we assumed, are characterized by eluvial (mesocatena 1), transitional-eluvial (mesocatenas 2 and 3), and trans-accumulative (mesocatena 4) conditions on the slope of the Stavropol' uplands. A small amount of information concerning the objects of investigation is given in Table 1; more detailed information is presented in [22].

The granulometric compositions of the soils were determined by N. A. Kachinskiy. Identification of minerals in the coarse (>0.05 mm) fraction was carried out by wet screening through a set of sieves after kneading of the soil sample in a plastic state. In order to avoid destruction of minerals and formations of an authigenic nature, we did not use chemical treatment in this process. The coarse fractions obtained were separated in bromoform ($d = 2.9$ g/cm³) into light and heavy components. Subsequently, the heavy fractions were separated according to magnetic properties into strongly magnetic, moderately magnetic, and nonmagnetic components with the aid of an electromagnetic separator. The mineral composition was investigated by means of the crystal-optics method with the aid of a MIN-8 microscope and a stereomicroscope from the OPTON firm. After selection of required quantities under a microscope, opaque ore and authigenic minerals were identified by x-ray diffractometry with the aid of a DRON-2 diffractometer (Fe-emission). Infrared spectroscopy was used to identify substances in microscopic quantities. The spectra obtained were checked on a Secord M-80 instrument and interpreted according to the work of Plyusnina [20].

Counts of minerals were carried out per 500 grains, with subsequent recounts of numbers in each subfraction within the soil fraction >0.05 mm. A similar method of analysis is used for mineral prospecting in alluvial sand [12]. We used it, with minor alterations involving further subdivision of fractions with respect to size: >1 ; 1-0.5; 0.5-0.25; 0.25-0.1, and 0.1-0.05 mm; this increased the precision of determinations of mineral content.

Results of Investigations. The granulometric compositions of macrocatena soils located in the water divides of the interfluvies reflect the presence of two groups of soil-forming rocks. Soils of mesocatenas 1 and 2 primarily have light-clay mud-coarse-dust, finely dispersed compositions, whereas mesocatenas 3 and 4 have heavy-loamy mud-coarse-dust compositions. In water-divide soils of macrocatenas, the abundance of the aliphite fraction (<0.01 mm) decreases from top to bottom. The variation in the abundance of this fraction in soil-forming rocks is monotone; it is characterized by a maximum in the middle portion of the macrocatena. The silt fraction is distributed throughout the macrocatena in similar fashion in all horizons of the soil profile. The abundance of the loessal fraction gradually increases downward along the macrocatena; it differs by a factor of two at extreme points. The upper part of the macrocatena is distinguished by elevated content of the fine-sand fraction.

Floodplain soils of the upper part of the macrocatena (mesocatenas 1 and 2) are somewhat lower in weight relative to soils of the water divide; in the lower part of the macrocatena (mesocatena 3), they are somewhat greater in weight or are almost geochemically indistinguishable from soils of the water divide adjacent to them. In the final analysis, the granulometric fractions in floodplain soils throughout the macrocatena are fairly uniformly distributed, in contrast to soils of the water divide.

Three groups of minerals and formations of different origin can be distinguished within the composition of the coarse (>0.05 mm) fraction of macrocatena soils (Table 2). The first group are clastogene igneous and metamorphic minerals, stable and relatively stable, which have been subjected to prolonged transport from eluvium of solid crystalline rocks to deposits of sedimentary marine origin and, subsequently, to deposits repeatedly reworked by continental deluvial processes.

This group of minerals is found in both older and younger deposits, in soils of eluvial to trans-accumulative landscapes. The distribution of minerals in this group, together with the group's qualitative and quantitative composition and typomorphic features, allow us to infer sources of material and subsequent distribution of material within the landscape [5].

The second group consists of minerals of chemogenic-sedimentary origin. The minerals of group are less stable during transport than those of the first group.

TABLE 2. Abundances of Fractions, Genetic Groups of Minerals, and Formations, in Fractions of Horizon A in Soils of Macrocatenas, %

Mesocatena (geo- morphol- ogical setting)	Abundance of frac- tion > 0.05 mm in soil, %	Light fraction				Heavy fraction			
		abund- ance in fraction > 0.05 mm	clasto- genic (Group I)	chemo- genic (Group II)	pedo- genic (Group III)	abund- ance in fraction > 0.05 mm	clasto- genic (Group I)	chemo- genic (Group II)	pedo- genic (Group III)
1 (water divide)	27,8	99,1	88,7	0,4	10,9	0,9	28,5	71,5	Not found
2 "	20,6	99,6	75,9	13,3	16,3	0,4	58,6	41,4	traces
3 "	11,6	98,8	99,6	0,2	0,2	1,2	61,0	38,4	0,6
4 "	14,1	98,0	96,3	2,1	1,6	2,0	72,5	26,8	0,7
1 (floodplain)	10,4	97,2	79,2	12,9	8,0	2,8	21,8	61,1	17,1
4 "	15,5	97,7	50,3	n.o.	49,7	2,3	92,9	1,50	5,6

TABLE 3. Portion of Clastogene Minerals of the Heavy Fraction in Soils of the Macrocatena, % of Total Clastogene Minerals

Meso- catena	Magnetite + titanomag- netite	Rhombic pyroxene	Horn- blende	Zircon	Andalusite	Epidote	Staurolite
1	0,7	8,1	Not found	2,4	27,2	27,4	1,1
2	4,6	4,4	"	0,3	43,1	17,6	1,0
3	5,2	12,9	7,0	4,0	25,7	15,6	1,3
4	6,7	18,4	16,4	9,6	11,7	14,6	Not found

Meso- catena	Disthene	Apatite	Garnet	Rutile	Tourmaline	Ilmenite	Chlorite
1	1,8	1,6	3,3	0,7	23,3	Not found	2,4
2	0,4	1,6	5,7	0,5	13,7	2,7	4,4
3	0,2	3,3	4,9	1,5	Not found	5,8	12,5
4	Not found	12,6	4,1	0,6	"	1,1	4,2

Finally, the third group combines authigenic minerals formed in soil as a result of pedogenesis and contemporary geochemical processes. They are unstable from a physical-chemical point of view and disintegrate fairly easily during physical action and changes in the environment.

An analysis of the distribution of the enumerated groups of minerals in soils of the macrocatena reveals definite patterns resulting from different geochemical processes taking place over the course of the formation and evolution of the landscape.

The group of clastogene minerals (Group 1) occurs in all of the investigated soils of the macrocatena. Among this group of minerals, disthene and staurolite have received special attention, since they are considered indicators of supply of material from the Russian platform [9, 10, 16, 18, 21]. They played a very important role in the Neogene paleobasin [9, 18]. The quantity of minerals belonging to Group I in the light fraction of soils decreases from the eluvial part of the macrocatena to the transitional part and then increases again in the trans-accumulative landscape (see Table 2); there is also a decrease in the portion of these minerals in soils of the floodplain as compared to the water divide.

The greatest diversity of clastogene igneous and metamorphic minerals occurs in the heavy fraction, where the abundance of this mineral group shows a tendency to increase downward along the slope of the macrocatena (see Table 2).

The portion of minerals of the heavy fraction of soil varies in a regular manner over throughout the macrocatena (Table 3). From the eluvial part of the landscape, with P-N-deposits of marine origin, to the trans-accumulative part, where Quaternary loesslike rocks of continental origin are abundant, the relative abundance of clastogene minerals of the metamorphic complex, including andalusite, epidote, staurolite, disthene, and tourmaline, decreases. The variation in the abundance of disthene and staurolite over the macrocatena suggest a substantial decrease in material from the Russian

TABLE 4. Abundances of Minerals and Formations in the >0.05-mm Fraction of Horizon A in Soils of the Macrocatena

Macro- catena geomorph- ological setting)	Clastogene (Group I)												
	quartz	Feld- spar	musco- vite	biotite	chlorite	magnetite + titanomag- netite	rhombic pyroxene	horn- blende	zircon	andalusite	epidote	staurolite	disthene
1.** (water divide)	65,2	21,9	0,8	Not found	0,6	0,2	0,2	Not found	0,6	6,9	6,9	0,3	0,5
2 "	38,8	28,8	7,9	"	1,1	1,1	1,1	"	0,1	10,6	4,3	0,2	0,1
3 "	56,7	32,0	8,3	1,4	8,3	3,4	8,5	4,6	2,6	17,0	10,3	0,8	0,2
4 "	64,0	23,3	5,5	2,4	3,7	7,5	20,8	18,5	10,8	13,2	16,5	Not found	Not found
1 (floodplain)	47,3	29,5	0,1	0,02	32,7	0,9	2,7	4,6	4,4	8,4	7,0	0,4	"
4 "	26,5	19,9	1,7	1,0	199,0	1,6	0,7	4,2	5,4	6,0	Traces	Not found	"

Macro- catena (geomorph- ological setting)						Chemogenic-sedimentary			pedogenic (Group III)				
	Apatite	garnet	rutile	tourmaline	Ильме- нит	limestone	Fe oxides	cherts (Fe)	water- stable aggreg- ates	fragments of mollusc shells	carbonate nodules	chlorite	Fe oxides
1 (water divide)	0,3	0,8	0,2	5,9	Not found	3,2	100,1	Not found	1078,0	Not found	Not found	Not found	Not found
2 "	0,4	1,4	0,1	3,4	0,7	600,3	736,8	"	1067,9	2,6	5,5	"	"
3 "	2,2	3,2	1,0	Not found	3,8	Not found	63,5	0,4	Not found	24,4	Not found	"	"
4 "	14,2	4,6	0,7	"	1,3	3,0	259,0	"	66,14	5,0	81,0	1,0	1,5
Not found	Not found	Not found	Not found	Not found	Not found	1089,0	332,5	0,1	165,0	0,6	Not found	597,9	Not found
4 "	"	"	"	"	"	Not found	3,5	Traces	3696,8	257,7	339,3	564,0	1,8

Explanation. Abundances of quartz, feldspar, muscovite, and biotite are given in percentages, other minerals in 10^{-2} %.

platform during the creation of the soil-forming rocks in the trans-accumulative part of the landscape on the southeastern slope of the Stavropol' uplands. Here, there are increases in the proportions of magnetite, titanomagnetite, rhombic pyroxene, hornblende, zircon, and apatite, which are characteristic of rock of the intrusive complex. The majority of these minerals are distinguished by freshness as well as absence of evidence of prolonged transport and weathering; this suggests proximity of the source of their supply. These characteristics are most pronounced in the case of rhombic pyroxene, which occurs in the form of idiomorphic crystals with magnetite inclusions. Magnetite, titanomagnetite, hornblende, rhombic pyroxenes, and micas can be singled out as characteristic of mineralogical provinces adjacent to the Caucasus [1, 2, 7, 24] and could probably serve as markers for deposits of terrigenous material originating from that region. According to our data, the presence of these minerals and their condition suggests a supply of terrigenous material from the Caucasus.

An analysis of the distribution of the first mineral group throughout the mesocatena indicates that the degree of dissection of the topography has a substantial influence on the ratio of minerals in the coarse fraction of soils in different geomorphological settings. In the soil of the floodplain, the eluvial, strongly dissected part of the macrocatena (Table 4, Mesocatena 1), there are minerals of low and intermediate physical-chemical stability (biotite, hornblende) not found in the soil of the water divide. In the coarse fraction of floodplain soil, there are also greater portions of such minerals as magnetite, hornblende, zircon. Apatite, garnet, rutile, and tourmaline do not occur here. These facts suggest active deluvial transport of material along the slope, exposure of slightly weathered soil-forming rocks, and involvement of their decomposition products in soil formation in the lower lying landscape.

In the floodplain soil of the trans-accumulative landscape (Mesocatena 4), with less dissected topography, there are lesser portions of all clastogene minerals, except chlorite, in comparison with the soil of the water divide; conditions here are favorable here for the synthesis as well as preservation of chlorite [28]. The noticeable decrease in the relative abundance of clastogene minerals is due to intensive creation of pedogenic minerals and formations here.

The group of chemogenic-sedimentary minerals (Group II) includes calcite composing limestone, silica, and various forms of iron oxides and hydrous iron oxides (limonite, goethite, and hematite).

Limestone occurs both in the form of stone gravel in water-divide soils of mesocatenas 1 and 2 and in a more dispersed state in the floodplain soils of these mesocatenas. Further along, in the trans-accumulative part of the macrocatena, the abundance of limestone fragments in the soils decreases substantially, whereas the dispersion and degree of roundedness of limestone fragments increases.

Iron oxides and hydrous iron oxides in the form of dense, rounded, and semirounded fragments of dark-brown, red, white, and yellow colors are primarily present in heavy magnetic and nonmagnetic fractions. In the light fractions, the iron oxides are lighter in color and frequently occur with inclusions of quartz, feldspar, and mica. According to our investigations and the investigations of other authors [11], chemogenic-sedimentary iron oxides and hydrous iron oxides are characteristic of marine P-N deposits. In the soils of the upper part of the macrocatena (mesocatenas 1 and 2), these formations are inherited from soil-forming rocks; their presence in soils formed on rocks of continental origin in the lower part of the macrocatena (mesocatenas 2 and 4) may indicate deluvial drift of material from the upper slope of the Stavropol' uplands.

An analysis of the distribution of minerals in the chemogenic-sedimentary group over the mesocatenas in comparison to soils of the water divides and floodplains and soils of floodplains reveals patterns associated with the present-day process of mechanical migration. In the coarse fraction of the floodplain soils of Mesocatena 1 (the eluvial part of the macrocatena), there is a greater proportion of the chemogenic-sedimentary group as a whole in comparison with the water-divide soil (Table 4). We found the same pattern above in the case of clastogene minerals with low and intermediate physical-chemical stabilities. The reverse trend was found in the case of Mesocatena 4 (trans-accumulative part of the macrocatena); this situation is a consequence of the great remoteness of the soils of this floodplain from the source of chemogenic-sedimentary material and the breakdown of such material during prolonged transport.

The group of authigenic minerals and formations (Group III), predominantly found in soils and associated with the origin of the soils, is present in the light fraction of loose carbonate nodules formed along pores and paths of roots, water-stable aggregates, and aragonite fragments of mollusc shells. The x-ray diffraction patterns and infrared spectroscopy suggest the presence of chlorite (chamosite), rock phosphate, iron oxides, and hydrous iron oxides of tabular shape and layer structure in the heavy fraction. Later formations are brown, black or yellow, occasionally with impressions of plant cellular tissue. The magnetic varieties are dense and dark-colored, with the metallic luster in their dense central portions characterized by a goethite-mahgemite composition. The nonmagnetic varieties of these formations are less consolidated and lighter; they are of a hydrogoethite composition. Goethite can be identified diffractometrically on the basis of the

following values of d/n , in Å: 4.98; 4.20; 3.34; 2.69; 2.45; 2.25; 2.19; 1.72. Magnetite can be identified by values of d/n , in Å: 2.96; 2.52; 2.09; -1.69; 1.61; 1.48.

In contrast to goethite, hydrogoethite shows strong, broad absorption in the infrared region ($\approx 3.200 \text{ cm}^{-1}$), suggesting the presence of hydrogen-binding OH-groups in the structure.

The quantity of authigenic carbonate formations is greater in soils of the trans-accumulative part of the macrocatena (see Table 4). Thus, the quantity of carbonate nodules in the coarse fraction of floodplain soil in the mesocatena is 4 times greater than in soil of the water divide. An analogous pattern is found in the distribution of authigenic ferruginous formations. In the eluvial part of the macrocatena (in soils of mesocatenas 1 and 2), we did not find these formations, but their existence was noted in soils of Mesocatena 3, and they are most abundant in Mesocatena 4.

In the group of authigenic minerals, we also include iron-chlorite (chamosite), which occurs both in the heavy and the light fractions, exhibiting a density apparently similar to that of bromoform. Grains of chamosite have tabular, isometric, occasionally lumpy shapes, dark green and green colors (frequently not transparent, with black carbonaceous inclusions), and low hardness; this rules out an allothigenous origin for these grains in the soils under consideration.

On x-ray diffraction patterns, the mineral can be identified on the basis of reflections with the following values of d/n , in Å: 14.2; 7.06; 4.72; 3.53; 2.45; 2.39; 2.12; 1.55. Strong reflections (7.06 and 3.53 Å) from a basal lattice with even rows suggest iron content. This mineral is paragenetically associated with accumulations of iron oxides in accumulative areas of the landscape [17]. We found iron-chlorites, in particular chamosite, in greatest quantities in floodplain soils (mesocatenas 1 and 4); iron-chlorites are found in lesser quantities in soil of the water divide of the trans-accumulative landscape (Mesocatena 4). Using the method of infrared spectroscopy, phosphate compounds can be identified here on the basis of a strong, broad absorption band with doublets at 1100 and 1052 cm^{-1} and triplets at 630, 604, and 570 cm^{-1} [18]. At first glance, there seems to be an unexpected absence of pedogenic magnetic species of iron oxides in coarse fractions of soil in the floodplain of Mesocatena 1, where there are fairly many authigenic iron-chlorites with which such species are paragenetically associated [28], but as investigation of the silt fraction has shown [3], iron oxides, including ferrous forms, are deposited on the floodplain in a very dispersed state. It is possible that local geochemical conditions prevent accumulation of the species we identified in the coarse fraction.

There is a predictable relationship between the distribution of authigenic mineral fluctuations over the macrocatena and the formation of water-stable soil aggregates. In the eluvial part of the macrocatena (mesocatenas 1 and 2), these aggregates are dark grey and do not break up under the action of 10% HCl; this suggests humus as the main glueing material. In transitional and, especially, trans-accumulative landscapes (mesocatenas 3 and 4), carbonate and ferruginous material begin to play an important role in the formation of water-stable structures, whereas iron compounds play an important role as an aggregating agent in the floodplain soil of Mesocatena 4.

Discussion of the Results of the Investigation. The mineral composition of the coarse fraction of soils, soil-forming rock, and underlying rock in the system of adjacent landscapes under consideration are determined by the developmental history of the territory and present-day soil-geochemical processes of breakdown, transformation, transport, and secondary synthesis of mineral components.

Analysis of the distribution of clastogene minerals indicates a supply of mineral from the Russian platform and the Caucasus. During the Quaternary, the latter became the main source of terrigenous material. The upper part of the slope of the Stavropol' uplands, composed of marine P-N deposits, formed from material which arrived mainly from the Russian platform. Kholodov et al. [24, 25] reached a similar conclusion after studying the clay minerals in the Middle Miocene deposits of Eastern Ciscaucasia. The younger Quaternary continental loesslike deposits, which occur lower in the topography, mainly contain terrigenous mineral supplied from the Caucasus.

In contrast to Balaev and Tsarev [4] as well as Galaya [7], who propose a supply of loesslike material from the side of the Caspian lowland via an eolian route, our data indicates a predominant role for a Caucasus source in the formation of loesslike rock. To a large degree, this is in agreement with the hypothesis of an aqueous-accumulative origin for these deposits. A similar hypothesis concerning the formation of soil-forming rock was proposed earlier by Kovda and Samoylova for the Russian plain [13, 14]. Considering the data of Ryskov et al. [22], it can be assumed that mainly mineral salts arrived via an eolian route; i.e., the sources of saline and terrigenous material for this territory were different. With increasing uplift of the Stavropol' uplands and regression of the Caspian basin, deluvial drift, probably travelling along the length of the slope of the basin, begins to exert an influence on the formation of loesslike deposits. The presence of rounded fragments of chemogenic-sedimentary iron oxides and hydrous iron oxides, limestone, and silicified forma-

tions, characteristic of neogenic deposits of marine sedimentogenesis, in loesslike rocks in the vicinity of mesocatenas 3 and 4 are evidence for such mechanical geochemical migration of material over a substantial distance.

Thus, the creation of soil-forming deposits in this territory proceeded both under the influence of geochemical mechanical migration** from the Stavropol' uplands and as a result of arrival of terrigenous material from the Caucasus.

Besides mechanical migration of material, this landscape is subjected to a group of geochemical processes resulting in decomposition, transformation, synthesis, and organization of mineral material, transport of such material by fluid surface and subsurface flow in the form of colloidal and true solutions. The directions and intensities of these processes depend upon the position of the landscape within the geochemical association. Processes of decomposition and evacuation of mineral components predominate in the soils of the eluvial part of the macrocatena. Lower along the slope of the macrocatena, weathering processes weaken and, to an increasing degree, are compensated for by supply of material from higher-lying landscapes. Under these conditions, the flow of material increases and transformation and new synthesis of mineral formations become substantial. This is expressed in the formation of carbonate nodules in soils of mesocatenas 3 and 4 as well as occurrence of authigenic iron oxides and hydrous iron oxides, iron-chlorites, and rock phosphate (Meso-catena 4), which is most substantial in the floodplain soil.

It is evident that the two identified groups of processes associated with the formation of mineral matter in soils of the geochemical landscape (mechanical migration and migration in the form of true and colloidal solutions) did not play equally important roles during certain periods of evolution of the landscape as a whole. In the landscape under consideration, one can thus identify a period when mechanical migration predominated, resulting in the creation of the mineral composition of loesslike soil-forming rock, and a period when migration of colloidal and actually dissolved material predominated, resulting in the decomposition and evacuation of mineral matter in eluvial settings and the formation of neomineralizations in soils of accumulative landscapes. The alternating predominance of one process over the other and the duration of each period depended upon climatic and tectonic conditions determining the evolution of the landscape as a whole.

The material presented persuasively shows that the mineral mass in each soil is a product of geochemical processes at different levels and is a result of the redistribution of material between mega-, macro-, and meso-landforms. The soils of this region exhibit geochemical ties between the Caucasus and the Ciscaucasian plains above all, between the top portion of the Stavropol' uplands and its slopes secondly, and, between the influves and floodplains dissecting these slopes thirdly. Pedogene minerogenesis occupies a definite place in this system of processes. Analysis of the minerals in the coarse fractions allows us to estimate the contribution of each hierarchical level to the formation of the mineral portion of the soils in Central Ciscaucasia.

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LITHOLOGICAL PROBLEMS, GEOCHEMISTRY AND PALEOGEOGRAPHY OF CENOZOIC DEPOSITS IN THE PRECAUCASUS.

PART 1. Interrelationship between Formation Conditions, Lithology and Geochemistry of the Maikop Deposits

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UDC 552.1:550.4(470.6)

Lithologic and mineralogical characteristics of the Central (Kuban' River) and Eastern (Sulak River) type sections of the Maikop Series have been studied in the Precaucasian region. Differences developed mostly during the depositional stage and reflect certain influences on sediment accumulation. Discharge of a large platform stream that deposited large sediment volumes, played a major role in sediment accumulation in the eastern Precaucasus.

The Maikop deposits of the Precaucasus represent a thick sequence of clayey and sandy-clayey rocks that formed during the Oligocene-early Miocene, at a time of relative tectonic quiescence. During this time, 22-23 Ma [20], the eastern Paratethys boundaries, within which the Maikop Series was deposited remained fixed and sediments had uniform characteristics over large areas of the basin [4]. Certain typical horizons (e.g., ostracode-rich layers of the Khadumsk Formation) can be traced for a distance of a hundred kilometers. At the same time, as the result of differences in basin floor characteristics in sediment volumes and sources, the Maikop deposits is played great facies variability.

Deep water basins, not filled in by sediments [17], as the Black Sea developed under hydrogen sulfide-enriched bottom water conditions, described for the Maikop Sea [1, 4, 7, 10, 12, 15, 18, 24]. Accumulation of thick sediment sequences under reducing depositional conditions led to organic matter- and pyrite-enriched sediments, often devoid of fauna; with characteristic geochemistry and high potential as petroleum source [12]. This unique character of the Maikop Series in the Precaucasus attracted increased geological attention.

Two type sections of the Maikop Series have been studied. The Kuban' River section is stratotype of the central Precaucasus area, while the Sulak River section reflects deposition conditions and postdepositional alteration of the Maikop beds in the eastern Precaucasus. During Maikop times, both sections accumulated near the Caucasian island and were characterized by similar facies conditions. At the same time, they reflect markedly different rates of sediment accumulation; differences between the northern (platform) and southern (Caucasian) sediment source areas, between postdepositional alteration styles, and other aspects. These differences impacted the lithofacies and mineralogical-geochemical sediment characteristics. Their mineralogical-geochemical sediment characteristics. Their recognition helps in defining formation conditions of the Maikop beds in the Precaucasus.

Kuban' River Section. Prokopov [14] was the first to describe the section and his subdivisions are still in use. The section contains the following seven subunits (upward): Khadumsk, Ol'ginsk, Batalpashinsk, Septarian, Zelenchuk, Karadzhalgin, and units. The lower four are Oligocene, the top three, of Miocene age [4, 15].

The **Khadumsk** Formation is subdivided into three distinct members. The lower (Pshekhsk Horizon) consists of greenish- and cinnamon-gray, thin-layer and indistinctly layered carbonaceous clays with fish fossils. The lower part of the Pshekhsk Horizon includes numerous broken, thin-walled *Planorbella* shells. In individual, maximum 1.5-2 m thick intervals thin dark layers are enriched in reworked organic matter that produced the typical moiré pattern of the slope. Very minor amounts of silty clay are present. Maximum 3-5-cm-thick volcanic ash layers with montmorillonite development occur. The clays generally smell of petroleum and include rare jet-lignite lenses. The thin middle Khadumsk

member (1.5 m) is an excellent marker horizon for are hundred kilometers. It is known as the Polbinsk, or Ostracode Marl. This light-gray, indistinctly layered marl includes numerous ostracode valves. The upper Khadumsk member was named Morozkina Balka. It consist of interlayered carbonates and carbonate-free, cinnamon-gray, indistinctly and finely layered clays.

The **Batalpashinsk Formation** consists of strongly altered, jarositized clays, with numerous gypsum crystals. Montmorillonitized thin volcanic ash layers are rare. 15-20 cm thick beds of carbonate concretions occur. Their number increases in are the upper part of the unit. The concretions are often found on or within wood fragments. Clays are practically absent from the silts.

The **Septarian Formation** consists of altered clays. In appearance and composition these are very similar to clays of the Batalpashinsk Formation and lithologically differ only in the presence of numerous septarian concretion layers. In the lower part of the unit the concretions are small (maximum 20 cm) and the septarian character is vague. The upper part includes large, typical cake-shaped septarian concretions of maximum 150-cm diameter. At the top of the unit the Alkumsk Horizon provides a typical marker bed. It consists of thin (5-6 cm) contorted layers of sandy marl that thicken laterally, forming maximum 1.5-2 m thick beds of concretions.

The **Zelenchuk Formation** represents a unique sandy interval. Its lower part consists of dense, massive sandy-silty micaceous clays with fish bones. At higher level maximum 1-cm-thick sand laminae occur. The upper part of the unit contains thin (maximum 0.5 m) beds of fine-to-medium-grained, occasionally poorly sorted, yellow, micaceous, unconsolidated paleosols. Their tops include isolated concretion bodies of the same sandstones. These are denser and well-cemented. 3-5-cm-thick sand dikes cut the sand layers. The upper sand beds are fractured and form a peculiar, coarse clay-sand breccia.

The **Karadzhalin Formation** contains clays with beds of siderite concretions. The clays are dark gray, occasionally cinnamon-gray and contain almost no silt. They are massively bedded and contain fish fossils. A characteristic feature of the clays is the unusual moiré pattern on bedding surfaces. Siderite concretions occur haphazardly throughout the unit. In the lower interval the unit they contains silt admixture and fish fossils; in the upper part, siderite alone. The concretion diameters usually range between 20-40 cm, reaching maximum 1 m.

The **Ol'ginsk Formation** contains cinnamon- and cinnamon-gray colored, indistinctly bedded silty clays, with almost no fish fossils. Small, granulelike sulfide concretions concentrate in the lower part of the unit. Sulfide mineralization occasionally proceeded along small worm tracks and burrows.

Sulak River Section. The lithology of Maikop beds in the Sulak River section differs significantly from that of the Kuban' section. The section is much thicker and sandy deposits are much better represented. Shatskii's classical stratigraphic subdivision [26] also contrasts with the Kuban' subunits. The Maikop Group is subdivided into six units; the Khadumsk, Miatlinsk, Lower Clay, Mutsidakal', Riki, and Zuramakent Formations.

The **Khadumsk Formation** contains dark-brown, almost black, very dense, bituminous, massive, carbonate-bearing clays with rare fish fossils and pyrite concretions. As in the Kuban' section, the middle Khadumsk also contains ostracode marl. The lower Maikop section on the Sulak River has been tectonically altered. Folding, numerous faults, and overthrusts hamper description of this formation.

The **Miatlinsk Formation** consists of sandy-clayey deposits. Generally fine- and medium-grained sandstones dominate in the lower interval. Along with dense sandstone layers of massive bedding, horizontally and wavy-laminated varieties have quite wide distribution. They are not strongly cemented and are often enriched in dark minerals and contain small clay and biotite-mica lenses and laminae. The clays are dark-gray and sandy. Many tectonic dislocations, bed duplications and small fold occur in the lower Miatlinsk Formation. The upper, sandy clay interval is massively bedded, and contains fish fossils. The sandstones occur only in beds, intercalated with clay layers. Individual beds are 1-15 cm thick. These parcels often are interlayered with fine-grained sandstones and gray clays.

The Miatlinsk beds are overlain by the Lower Clay Horizon that consists of gray, massive or indistinctly layered, occasionally foliated slats. The clays usually are clean. In a number of instances they display moire pattern, similar to clays of the Karadzhalin Formation in the Kuban' section. Thin layers and lenses of light-colored sandstones, often enriched in dark minerals occur occasionally in the upper interval. In contrast with the gray clays, cinnamon-colored massive clay beds are present, without fish fossils.

The **Mutsidakal' Formation** represent interlayered clays and sandstones. The sandstone distribution area small. The gray clays belong to two categories: laminated, without any fossils; and denser, with fish fossils and weakly expressed *moiré* (irregular wavy) pattern. The upper part of the sequence includes cinnamon-brown, massive, nodular, very dense sandy clays. The sandstones are yellowish-white, fine-grained, often bituminous, occasionally with wavy or lenticular layering. Occasionally, the sandstones appear as irregular lenses and blocks, forming dikes that crosscut bedding surfaces [26].

The thick Riki Formation Overlies the Mutsidakal'. The dark gray, dense pure clay, includes practically no silty admixtures and contains fish fossils. During weathering the clays disintegrate into ash-gray, thin laminate. The lower part of the formation contains few beds of large septarian concretions. Thin layers and small lenses of light colored, fine-grained sandstones persist. Siderite concretions are common in the upper part of the formation.

Zuramakent beds complete the Maikop sequence. They include indistinctly layered greenish-brown clays, with blue-tinted siderite concretion layers, with pyrite crystals near the surface. The clays display worm trails and rare fish fossils. The upper part of the formation includes dense, dark gray, laminated clays, rare worm trails and layers of spherical septarian concretions.

Due to the paucity of enclosed fossils, the Maikop beds unfortunately display few stratigraphic reference levels. The large Maikop distribution area and facies variability precluded formulation of a uniform biostratigraphic system. For this reason, correlation of the sections is fraught with uncertainties. Only the Khadumsk Formation offers good correlation. The previously discussed Batalpashinsk Formation that, as defined by Prokopov, includes the Septarian unit, according to Somov [16] corresponds to Shatskii's Miatlin-Mutsidakal' beds. The Zelenchuk and Karadzhalgin Formations are approximate correlatives of the Riki Formation; the Ol'ginsk and Rits Formations correlate with the Zuramakent Formation [8, 27].

The discussed sections of the Maikop Series have been sampled in detail. These samples were subjected to microscopic, x-ray, and chemical analyses.

Clay plays a key role in the formation of Maikop beds, partly in the Sulak River section, and in particular in the Kuban' River section. Sand beds do not exceed 5% of the total thickness of the Sulak section. Sand bed ratios do not exceed 1% in the Kuban' section. Mineralogical-geochemical aspects therefore carry vital information on the deposition and paleogeographic conditions of the Maikop Basin. Eight type samples from the Kuban' section, ten from the Sulak section were taken. The samples, picked at approximately even intervals, were used to establish the clay mineralogy of the sequence. The samples first were fractionated by elutriation. X-ray study of the <0.001-mm fraction followed in the Laboratory of Physical Methods, GTN, Russian Academy of Sciences. The clay fractions of the Maikop deposits of the clay minerals included smectite, mixed-layer mica-smectites, micas, illite, chlorite, and kaolinites. The Bradlin-Biscaye method provided approximate mineral ratios in the samples. Smectites and mica-smectites, conditionally are referred to as *smectitic components*, while micas and illites as *mica components* (Table 1). Because only semiquantitative results have been received, the calculations fail to reflect accurate clay mineral ratios in the rocks. Nevertheless, in using "greater than" and "less than" designations, the values, based on qualitative shifts in the ratios provide changes in the trends of these interrelationships [22].

The interrelationship between clay minerals in the Kuban' section is representative of the entire section. Mica is the main component, followed by smectite, chlorite, and kaolinite as secondary. Only the upper part of the section contains increased smectite content and correspondingly reduced concentrations of mica components. All analyzed samples contained these components.

The distribution pattern of clay minerals is known better in the Sulak section. The smectitic mineral content declines upward in the section. In the lower section this fraction is a mixed-layer mineral that forms a one-layer complex when treated with glycerine. In the upper section this fraction is represented by finely dispersed, poorly ordered smectite. Typically, upward in the Sulak section chlorite gradually disappeared from the clay minerals of the Maikop deposits. At the same time, the kaolinite content displayed a minor but marked increase.

Two aspects are essential in comparing clay mineral ratios in the Maikop clays of the studied sections. First, in clays of the Sulak and Kuban' sections the total chlorite-kaolinite percentage values are quite close. They approximate 20% of the total clay mineral content (Table 1). While all samples from the Kuban' section included chlorite and kaolinite, samples from the upper half of the Sulak section contain no chlorite. Therefore, the kaolinite content increases upward

TABLE 1. Clay Mineral Composition in the <0.001-mm Fraction

Sample number	Smectite	Mica	Chlorite and kaolinite	Sample number	Smectite	Mica	Chlorite and kaolinite
Kuban' river				Sulak river			
158	30	55	15	360	—	85	15
163	20	55	25	374	—	95	5
180	10	70	20*	390	5	75	20
190	10	70	20	397	—	65	35
204	20	55	25	398	5	75	20*
216	35	50	15	414	5	80	15*
222	30	45	25	421	—	70	30
234	35	40	25	444	10	70	20*
Mean	25	55	20	466	15	50	35*
				474	10	65	25*
				Mean	5	75	20

Note. Smectite includes also the mixed-layer mica-smectite minerals.

*Chlorite absent from sample.

in that section. Second, the ratios of mixed-layer and mica components are markedly different between these sections. In the Kuban' section the mixed-layer content is greater, the mica content correspondingly less than in the Sulak section. In the Sulak sequence the mixed-layered mineral content clearly increased upward.

Chemical and spectral analyses of the Fe, Mn, Ti, P, Cr, V, Ni, Co, Pb, Ga, Ge, Ma, Cu, C_{org}, and CO₂ content were used in identifying geochemical aspects of Maikop deposits. Studies were undertaken at the Chemistry Laboratory, GIN, Russian Academy of Sciences. 61 clay and 16 sand samples were analyzed. The arithmetic mean chemical element content was calculated for each formation and for sand and clay intervals of the sequence, in general. In addition, variation coefficients and paired correlation coefficients have been calculated (Tables 2 and 3). Correlation coefficients are graphically shown in Figure 1. Thick lines display the five most significant correlation ties, while thin lines and dots indicate other significant correlation ties at the 1% and 5% levels of significance.

Table 2 reveals distinctions between the chemistry of the two groups. Cr, V, Ga, Ge, and Ti predominate in clays of the Sulak River section, while Ni, Cu, Co, Pb, Mo, Fe, P, and organic C dominate the Kuban' River section. Most elements in the sections display very minor differences in mean concentration values and cast doubt on to the validity of the group designations. However, further statistical analysis of the data confirmed the cited pattern.

First, in each section elements were ranked by increasing variation coefficient values:

Sulak River: Ti, V, Ge, Cr, Ga, Co, Pb, Cu, Ni, Fe, P, C_{org}, Mo, Mn, CO₂

Kuban' River: Ge, Ti, Ga, Fe, Pb, Cr, V, Ni, Co, Cu, C_{org}, P, Mo, Mn, CO₂

Elements in the first group (Ti, V, Ge, Cr, Ga) occur on the left of the sequence. They display a minimal dispersion pattern of the concentration values and the variation coefficients do not exceed 20%, occasionally, 25%. Elements of the second group occur in the right side of the sequence. Two subgroups occur. The first includes Co, Pb, Cu, Ni, and Fe. Their variation coefficients ranged between 20-50%. The second subgroup includes C_{org}, P, Mn, Mo, and CO₂. Their dispersion was greater and the variation coefficients exceeded 50, 100, even 200%.

Subdivisions of elements is best established in the Sulak River section. Five elements of the first group occupy the first five positions in the variation sequence. In the second group the maximum variation coefficient value was 19%; the minimum, 29%. The boundary between the subgroups occurs at the 70% level. Group separation was less pronounced in the Kuban' River sequence. Along with Ti, Ge, Ga, V, and Cr; Fe and Pb also belong to the first group. The variation coefficient values are somewhat higher (maximum: 25%). Maximum variation coefficients of second group elements were smaller than these values in the Sulak River section. The boundary between subgroups of the second group occurs at the 50% level.

Second, element groupings became clearly observable during compilation of correlation diagrams (Fig. 1). Two discrete chemical element groups are visible in the Sulak section diagram. The first includes V, Ga, Ti, Ge, and Cr. Among the two subgroups of the second group, the first includes Fe, Co, Ni, Pb, Mn, P, and the separate CO₂. The second subgroup includes C_{org}, Mo, and Cu. The Sulak section diagram shows that each of the 15 studied components

TABLE 2. Mean Composition and Variation Coefficients of Chemical Elements in the Maikop Deposits, Sulak and Kuban' Type Sections

Section rock type	Cr	Ni	V	Cu	Co	Pb	Ga	Ge	Mo	Fe	Mn	Ti	P	C _{org}	CO ₂	Sample number
	10 ⁻⁴ %									%						
Mean content																
Kuban' river clays	97	88	170	68	23	21	22	2,2	20,8	4,53	0,05	0,52	0,03	1,24	0,69	26
sandstones	17	13	16	16	5	6	5	1,7	2,7	1,40	0,02	0,12	0,01	0	0	2
Sulak river clays	101	63	175	66	18	17	25	2,4	19,3	3,45	0,05	0,54	0,03	1,08	1,26	35
sandstones	61	32	69	19	12	11	9	1,6	3,5	2,76	0,07	0,38	0,04	0,46	2,18	14
Variation coefficient																
Kuban' river clays	24	31	25	43	38	23	16	10	83	22	85	14	71	50	199	
Sulak river clays	18	48	17	47	29	41	19	17	125	50	158	15	70	80	375	
sandstones	28	69	30	15	70	39	24	29	102	75	168	22	67	101	204	

TABLE 3. Mean Composition of Chemical Elements in Formations of the Maikop Series

Formations	Cr	Ni	V	Cu	Co	Pb	Ga	Ge	Mo	Fe	Mn	Ti	P	C org	CO ₂
	10 ⁻⁴ %									%					
Sulak river															
Khadumsk	49	35	119	58	17	14	11	1,9	42	3,63	0,06	0,32	0,07	1,76	20,57
Khadumsk *	92	103	223	109	32	26	21	3,4	79	6,81	0,11	0,60	0,13	3,30	—
Miatlinsk	109	42	189	44	15	13	28	2,7	34	2,65	0,02	0,58	0,02	1,12	0,06
Lower clay	102	55	157	71	17	22	26	2,5	10	3,73	0,05	0,61	0,03	0,58	0,07
Mitsiadakal'	106	51	165	49	19	20	24	2,3	10	4,13	0,07	0,61	0,03	0,46	0,15
Riki	97	65	187	78	19	15	25	2,3	32	2,52	0,03	0,53	0,02	1,38	0,21
Zuramakent	112	60	193	72	20	16	26	2,6	3	4,04	0,11	0,50	0,03	1,49	0,04
Kuba' river															
Khadumsk	82	81	178	70	17	19	19	2,2	19	4,47	0,05	0,45	0,03	2,17	3,67
Batalpashinsk	86	76	163	75	22	23	22	2,3	41	4,17	0,05	0,47	0,03	1,36	0,46
Karadzhalgin	94	95	151	81	22	24	23	2,2	17	4,38	0,04	0,54	0,02	0,86	0
Ol'ginsk	126	116	195	49	36	21	21	2,2	2	5,74	0,10	0,61	0,07	0,42	0,40
Ritsevsk	132	90	196	55	31	15	25	2,0	2	5,37	0,09	0,64	0,06	0,69	0

*Recalculated to carbonate-free composition.

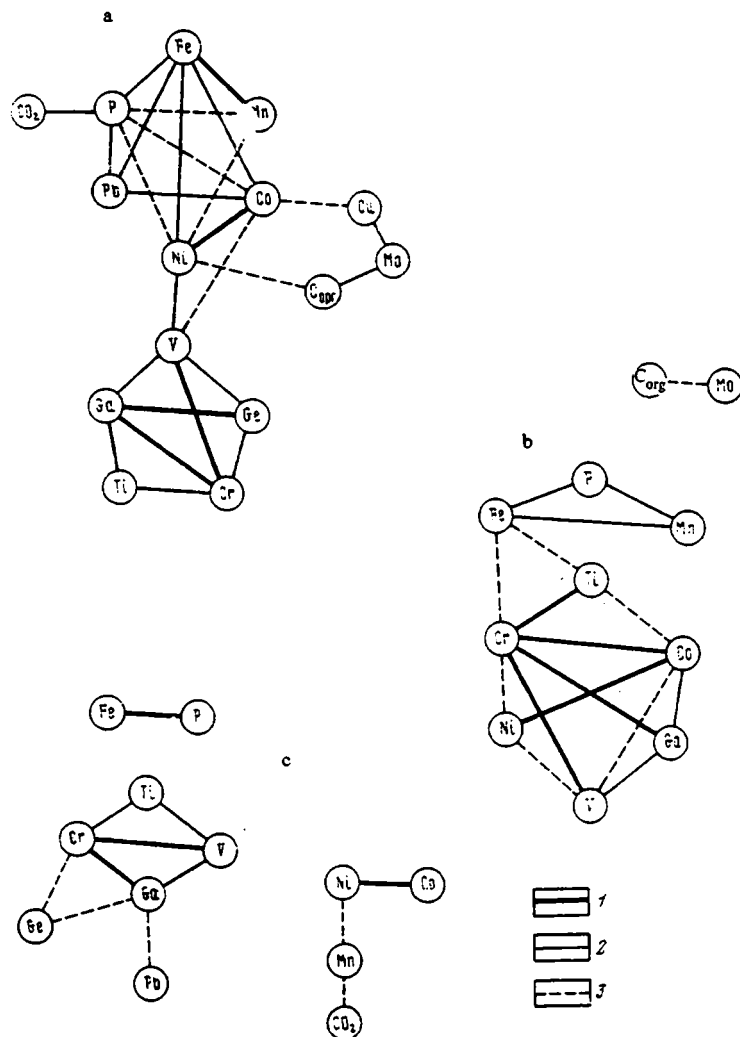


Fig. 1. Clay correlation diagrams, Sulak River section (a) and Kuban' River section (b), and sandstones in the Sulak River section (c): 1) the five most significant correlation ties; 2) significant correlation at 1% level; 3) significant correlation at 5% level.

TABLE 4. Stagnation Coefficient Values (Mo/Mn) in Formations of the Maikop Series along the Kuban' and Sulak rivers

Formation	Stagnation coefficient	Formation	Stagnation coefficient
Kuban' river		Sulak river	
Khadumsk	0,038	Khadumsk	0,070
Batalpashinsk	0,082	Miatlinsk	0,170
Zelenchuk	0,085	Lower clayey	0,020
Karadzhalgin	0,036	Mutsidakal'	0,014
Ol'ginsk	0,002	Riki	0,106
Ritsevsk	0,003	Zuramakent	0,003

possesses one significant correlation tie, not only at the 5% level but also the 1% level of significance. Additionally, when individual elements in the groups display significant correlation ties between element groups and subgroups at the 5% level, these correlations cease at the 1% level of significance and the groups become completely separate.

The correlation diagram of the Kuban' section differs significantly from the Sulak diagram. First, significant portion of the second element group (Cu, Pb, CO₂) generally does not display strong correlation ties even at the 5% level. No sharp separation occurs between elements, such as between the earlier described element groups. While C_{org} and Mo

represent a separate group, at the higher, 1%, significance level the other elements were subdivided into two groups. The first includes essentially V, Ga, Cr, and Ti; the second, Fe, Mn, and P.

In addition to these statistical parameters of element concentration patterns in the Maikop clays, the mean chemical element composition values have also been calculated for each formation.

The calculation revealed a haphazard pattern of element concentration changes upward in the section (Table 3). Most elements displayed no upward trend of concentration changes in Sulak section clays. Only a distinct, although very minor trend of Ni, Co, to a lesser extent, Cu-increase was noted, while the Ti content decreased slightly. As shown in the following, the Mn content, and to a greater extent the Mo concentration, increased sharply in the upper part of the Maikop beds (Zuramakent Formation) was not accidental. Due to the diluting effect by carbonates, well represented in the Khadumsk clays, elements of the first group displayed relatively low concentrations in the Khadumsk Formation. When recalculated to carbonate-free composition (Table 3), the concentration values of elements in the first group are nearly uniform throughout the entire section. However, after recalculation anomalous high concentrations of certain elements of the second group were noted in the Khadumsk Formation.

The Fe, Mn, Ti, P, Cr, V, to a lesser extent, the Co and Ni content increased in the two upper formations of the Kuban' section. Minimum C_{org} , Mo, and Cu values are typical of these formations. During quantitative evaluation of the degree of uniformity and differences in elemental concentration changes between the Kuban' and Sulak sections were identified in eleven satisfactorily correlated intervals. Along with paired correlation coefficient values, mean concentration values of the chemical elements have also been calculated. Significant levels of correlation between the same elements in different sections exist for Fe, Mn, Cr, and Ga. Only Fe and Mn displayed improved correlation at the 1% significance level. Unfortunately, correlations of sections within given intervals were inconclusively as the geochemical results may have been distorted in the process. There is a clear contrast between the Sulak and the Kuban' in the behavior of most chemical elements.

In sandstones, the mean elemental content of practically all components often was significantly higher in the Sulak section (Table 2) than in the Kuban' section. Only in a very thin intervals in the Zelenchuk Formation was the sandstone section analyzed. Statistical calculations are unavailable. a correlation diagram has been compiled for the Sulak section (Fig. 1), along with a component sequence that shows increased variation coefficient values for Cu, Ti, and Ga, Cr, Ge, V, Pb, P, Ni, Co, Fe, C_{org} , Mo, Mn, CO_2 .

If the unusual status of Cu is disregarded, elements in sandstones and clays displayed a clear-cut separation into the first element group, characterized by a maximum 30% variation coefficient of chemical elements, and the second group, with two subgroups. The first includes Pb, P, Ni, Co, and Fe, with a variation coefficient of 75%, and C_{org} , Mo, Mn, CO_2 , with a variation coefficient of 100%. The correlation diagram displays only the first element group. Components of the second group showed only few correlation relationships, or none.

The reviewed lithological and mineralogical-geochemical patterns of the investigated central Precaucasian (Kuban' River) and eastern Precaucasian (Sulak River) sections indicate many significant differences. In the following, we attempt to analyze these characteristics and the reasons for them. Sedimentary and postdepositional processes may account for these differences. Clearly, only diagenetic and initial katagenetic processes impacted the sediments. The depositional stage therefore played a decisive role in formation of the Oligocene–Miocene Maikop beds.

In the Maikop deposits characteristic aspects of clay mineral distribution were associated mostly with geographic locations of the investigated sections in relation to the main sediment source. This was clearly shown by the behavior of essentially allogenic chlorite and kaolinite [23]. The Malkinsk iron ore deposits and the surrounding area of extensive chlorite rock development in the Caucasian island center represented important chlorite sources for the Tertiary paleobasins. Eroding Jurassic deposits of the Caucasus similarly provided source sediments. Kaolinite was derived mostly from the Russian Platform. Under a hot and humid climate and in the relative absence of tectonism, the southern part of the Platform has undergone peneplanation during the Oligocene. Kaolinitic weathering horizons developed.

By taking into account the chlorite and kaolinite ratios on sediments derived from the Caucasus and Russian Platform, the continuous presence of chlorite in clays of the Kuban' section in the central Precaucasus reflects the marked influence of sediments, derived from the Caucasian island. The smaller role of chlorite in clays of the Sulak section and its complete absence from the upper part of the sequence, along with a minor ratio but persistent increase in the kaolinite ratio upward in the sequence, apparently point to the reduced volumes of Caucasian sediments during deposition. This also reflects increased development of kaolinitic weathering horizons on the Platform. The pattern of sediment transport from the Russian Platform [17] to the Maikop Basin, in general, has been investigated. When considering kaolinite and chlorite

distribution patterns in the Sulak and Kuban' section during sediment accumulation, it appears that a major stream, located in the eastern Precaucasian area, was instrumental in transporting sediments from the Platform area to the sea. The paleogeography of that region contrasted with that of the central Precaucasus.

The smectite and mica ratios in clays of the investigated sections indicate two characteristics. First, clays in the Kuban' section were relatively enriched in smectitic and depleted in illitic components. Second, the smectite components markedly increased in the Zoramakent Formation, upper Sulak section, from 0-5%, to 10-15%. A corresponding mica depletion from 70-90%, to 50-70% also took place (Table 1). The first change resulted from differences in the sediment volumes, attributable to different sediment sources. These sediments were derived from the central and eastern Caucasus. The second change apparently was caused by postdepositional clay mineral alteration and illitization.

Kholodov [21, 22] indicated the wide depth range of the illitized zone (1200-3700 m) and its variability in relation to changing facies-mineral conditions of source rocks, temperature gradients, and geobarometry in the region. Pt-conditions, required for katagenetic alteration of clay minerals, particularly for massive changes of the smectitic component in illite and mica, in the Sulak River area occurred at 3700 m depth. This depth is near the Zoramakent-Riki formation boundary. The depth required for massive illitization of clay deposits coincided with the depths of the chalky beds [2]. Maikop beds did not extend down to this level in the Kuban' section.

Predominance of platform-derived sediment matter greatly impacted the clay mineralogy of the Salak section. The sediments also reflect illitization. Illite formed from clays in the lower part of the section and did not influence Maikop beds in the Kuban' section.

Katagenetic illitization and dehydration processes in thick Maikop clay sequences of the Sulak section also explain formation of peculiar sandy structures that occur in the middle portion of the Sulak section. These are sandy blocks, lenses and dikes that cut across bedding planes [26]. The study of these features in Maikop and Middle Miocene deposits indicated that water, expelled under high pressures during dehydration was forced into sand beds [21, 22]. Quicksand formed. A sand slurry was intensively injected along zones of weakness into the enclosing clays beds. Blocky and dike bodies, or characteristic "inclusion horizons" developed, as the result [21].

Similar deformed sand layers also developed in the Zelenchuk Formation of the Kuban' section. However, Maikop deposits of this section were not buried at depths required for massive katagenetic liberation of water at depth. Water-saturation of the sand horizon and its subsequent deformation, therefore occurred during the depositional phase before sediment consolidation. The fact that sandstones of the Zelenchuk Formation formed alluvial fans illustrates this circumstance. Sediments were laid down by the rivers that drained the Caucasian island. The high deposition rates of the alternating sand and mud layers, as well as the relatively steep depositional slope, characteristic of alluvial fans, led to the deformation of liquefied sand beds and development of cross-cutting layers, such as just described.

Differences in geochemical characteristics between the Maikop sections are considered next. Differences in deposition conditions and in the intensity differences in postdepositional alterations defined differences in the clay mineral spectra. The first element group clearly, although not overwhelmingly dominates clays in the Sulak section. In the Kuban' section the second group displays concentration values, somewhat higher than the first. These element groups were not coincidental features. Three element groups were based on the conduct of chemical elements on the Black Sea floor [19]. The first includes Ti, Zn, Ge, Cr, and V. These geochemically more stable elements were transported in suspension. The elements accumulated along basin margins near their source area. The geochemically more mobile second group includes Fe, Mn, Ni, Co, Cu, Mo, W, As, Se, P, and CaCO_3 . These elements are transported in solution and as colloids, and accumulate only in pelagic basin areas. The third group includes Pb and Zn and resemble in behavior the second group randomly distributed throughout the basin. The two element groups of the Maikop Basin coincide perfectly with groups that were identified by Strakhov [19]. Thus, geochemical association of the chemical elements reflect loose relationships between elements. The most mobile elements became grouped already during sediment transport. Separation into groups becomes more intensive in the final medium of sediment deposition. The geochemically less mobile elements were associated with silty and coarse-pelitic suspension fractions [23]. Due to mechanical fractionation of the suspendates in the basin, they settled relatively close to terrigenous sediment sources, while the geochemically more mobile elements concentrated at substantial distances from the sources.

In contrast with the Kuban' section, the greater concentrations of geochemically less mobile elements in clays of the Sulak section therefore point to the proximity of mature terrigenous sediment sources. Because both sections were located near the Caucasian island source and the transport distances were approximately equal, the higher concentrations of the first element group indicate Russian Platform influences. This is also shown by the greater differentiation of sedimenta-

ry matter in the Sulak section. In comparison with a diagram and correlation sequence from the Kuban' section, the geochemically less mobile elements are more isolated in the correlation diagram and in the sequence of gradually increasing variation coefficients obtained from the Sulak section.

During the Oligocene, the terrigenous matter in the absence of tectonism and under a hot, wet climate on its way to its final area of deposition south of the Russian Platform, has undergone primarily chemical and lesser physical weathering. The sediments were repeatedly reworked. Depending on their mobility, the differentiated sediments reached a high degree of maturity when reaching the end of their transport route. They underwent final differentiation in the Maikop Basin. Caucasian terrigenous matter was transported only a very short distance to its site of deposition in the Sulak and Kuban' sections near the Caucasian island. As a function of the degree of mobility, this circumstance hindered element fractionation.

In contrast with the Kuban' section, geochemical characteristics of clays in the Sulak section indicate predominance of platform matter and mark the proximity of the section to the Russian Platform source area. Large streams drained the Platform and were instrumental in sedimentation processes of the eastern Precaucasus. The streams had a great impact on the Maikop Basin.

The variation coefficient values of element concentrations in the first group of the Sulak section are lower than those of the Kuban' section. Due to the more prolonged mechanical fractionation in the Kuban' section, more distinct from the Platform source area, the dispersion coefficients would be expected to be lower in the first element group. However, the higher variation coefficient values point to the influence of Caucasian sediment influx. Variation coefficient relationships in the first element group thus indicate significant impact of platform sediments in the Sulak section.

The dominance of platform-derived matter in the Sulak section and the influence of Caucasian island on sediments of the Kuban' section area is indicated by correlation diagrams (Fig. 1). In the first example, all elements, especially elements of the first group are associated with at least one other element at the 5% or 1% level of significance. Great similarities exist between concentration variation patterns of elements within a section.

For elements of the first group that are associated with suspendates of mostly coarse-pelitic and silt fractions, the similarity reveals a uniform source area. Similar concentration ranges in the second group developed mostly after deposition and reflect the intensity of diagenetic and katagenetic processes. Not all elements display mutual correlations in the second group. Although elements of the first group reveal a diagram pattern that resembles the Sulak configuration, the correlation between element concentrations became weaker, while Co and Ni became integrated into the group. Evidently there was a relative increase in sediment supply from the Caucasian island to the Kuban' section. Sediment mixing with platform matter weakened correlation between elements of the first group. Weakened ties between elements of the second group, on one hand reflect the increased concentration of Caucasian matter in the sediments. On the other hand, they indicate lesser degree of postdepositional alterations, when compared with the Sulak section.

Conclusions on ratio differences between the Russian Platform and Caucasian sediments in the Sulak and Kuban' beds are supported by the practical absence of any correlation between the concentration of the same elements in the sequence. Significant correlation exists between Fe/Mn; to a lesser extent, between Cr and Ga. Had the eastern and central Caucasian areas received sediments from the same source, there would be a correlation between changes in the concentration patterns of each element in the sediment sequence. The lack of correlation points to two unequal sediment sources. Correlation between Ga and Cr, elements of the first group that reflect platform influences, indicate overall dominance of platform sediments in the Maikop beds. As will be shown, the similar conduct of Mn in both sections of the sequence resulted from changes that affected bottom water gas regimes.

Upward in the sequence, the Sulak section displays a well-defined pattern of element concentration variations. Chemical elements have apparently been gradually added to the section. The upper two formations in the Kuban' section, the Ol'ginsk and Rits, displayed marked increase in the Ti, Cr, V, Fe, Mn, and P content and declining C_{org} , Cu, and Mo concentrations.

Increased Ti, Cr, and V, to some extent also Fe content in clays of the Ol'ginsk and Rits Formation was accompanied by increased coarse pelite and silt ratios in the sediments. This was probably due to an increased terrigenous sediment supply from the platform areas. However, sediment transport from the Caucasian island did increase earlier, in middle Maikop times. Sand then was deposited by the Kuban', Laba and many other west Caucasian streams. In the late Maikopian, the Kuban' River region experienced increased terrigenous sediment supply from platform areas. Because in late Maikop times the upper Sulak River section did not receive a greater influx in elements, stream sources must account for the additional sediment matter. The river mouths were located in the central Caucasus area. Research in the paleo-Don

region indicated that significant amounts of terrigenous matter were transported to the area of Stavropol' Arch in earliest Middle Miocene times [11].

A sharp increase in the Mg content and an equally abrupt decline in Mo concentration in the upper Maikop interval were definitely not coincidental. As noted, many researchers noticed hydrogen sulfide influx to Maikop Basin waters. Evidence for this was found in the upper Khadumsk Formation [4]. The greatest impact was felt in late Oligocene and early Miocene times [10, 15]. Hydrogen sulfide infusion was believed to have continued until Tarkhansk times [10]. The peculiar depositional conditions of H₂S-rich bottom waters were imprinted on geochemical sediment characteristics. The stagnation coefficient; the Mo/Mn ratio, is its most relevant geochemical indicator in the basin [24]. H₂S enrichment of bottom waters led to Mo precipitation from solutions and Mo accumulation in the sediments. Mn precipitates and Mo remains in solution in well oxygenated water columns. Gas content change on basin waters leads to abrupt Mo and Mn concentration changes in the sediments. A large body of data proves that when the ratio amounted to a few thousandths of unity, waters were well oxygenated. Hydrogen sulfide enrichment is indicated when the value exceeds one hundredths of unity. Table 4 displays stagnation coefficient values in the Maikop formations. A sharp drop in the values suggests a switch from H₂S-saturation to well-oxygenated conditions in the Kuban' section at the boundary between the Karadzhalginsk and Ol'ginsk Formations. Similar conditions prevailed in the Sulak section; the stagnation coefficient abruptly changes at the Riki-Zuramakent formation boundary. The absence of hydrogen sulfide influence in late Maikop beds is also indicated by observations made in worm trails, rare gastropod and bryozoa fossils in deposits of the Zuramakent (Sulak River), and Ritsev (Kuban' River) Formations in the upper Maikop sequence. The switch from hydrogen sulfide to oxidized medium is apparent in both sections at the same stratigraphic level. Thus, the change involved a large area in the eastern and central Precaucasus at the same time.

Chemical element groups thus evolved during sedimentation stages. At the same time, a grouping of elements, better defined in terms of their mobility, led to their postdepositional reorganization. Geochemically more mobile elements regrouped in the process. Diagenetic carbonate formation led to correlation between P, Mn, Fe, and CO₂. Sulfide development resulted in strong correlations between Cu, Ni, Co, Pb, and Mo [23].

Diagenetic processes affected Maikop deposits in both sections. However, separation of elements in the second group was more clear-cut in the correlation diagram and the variability sequence of the Sulak section. Katagenetic mica-forming and clay-dehydration processes apparently were responsible for the separation. As the result, large volumes of active fluids were segregated and expelled, leading to redistribution and strengthening of ties between elements of the second group. This also resulted in isolation of elements of the second group and its subgroups.

The geochemistry of the Maikop sandstones is less informative. Concentrations of almost all of the chemical elements in sandstones of the Sulak River section were slightly higher than in sandstones of the Kuban' River section. Without doubt, the Caucasian island was the main sand source in both instances. This is indicated by the sand facies distribution pattern near the Caucasian island, angularity of sand grains, as well as by terrigenous mineral data [6]. However, discharge from the Russian Platform may have also influenced the Sulak River section. Coarse terrigenous matter from the Platform was transported over great distances toward the south [3]. Zelenchuk Formation sandstones along the Kuban' River represent remnants of alluvial fan deposits, discharged from the Caucasian island. This is proven by the northward wedgeout of the sand unit, its thinness and isolated position. The element concentrations in sand fractions of both groups are much smaller than in the silt and clay fraction. In sands, the element content is relatively higher in both groups in contrast with their ratios in the mud fractions. Relatively increased concentrations of the first element group in sandy deposits of the Sulak section may indicate the impact of silty matter from the Russian Platform, or the better sorting and export of mud-size fraction from alluvial sands in the Kuban' section. At the same time, the greater element concentrations in the second group may have resulted from dehydration and subsequent liquid phase expulsion; redistribution and transport of a number of chemical elements from Sulak clays to sandy reservoir beds.

* * *

The interrelationship between clay minerals and the chemical element distribution characteristics in the Maikop Series in central and eastern Precaucasian type sections indicate that the basic mineralogical-geochemical characteristics of the Maikop rocks were associated with sediment deposition. As previously noted [17], the Russian Platform was the dominant sediment supplier to the Maikop Basin. The role of the platform as the primary source also featured in sediment budget calculations for the neotectonic stage that extended from the Late Sarmatian through the anthropogenic period [9],

and in calculations involving the Middle Miocene [23]. Sediments of Caucasian provenance represented less than 20% of the total in the Miocene. In Maikop times, the area of the Caucasian island was smaller than subsequently. The ratio of Caucasian sediments, therefore was even smaller then; maximum c. 10-15%. Naturally, south of the island the ratio of Caucasian matter in the basin was somewhat higher. This fact, however, applies in particular to the sand and silt fractions. Due to its great mobility, clay was disseminated throughout the entire basin. This resulted in the predominance of platform-derived sediments even along the periphery of the Caucasian island.

The impact of the Russian Platform, with an overall dominance of platform matter in Maikop deposits, was much greater in the eastern Precaucasus (Sulak River). A number of facts point to this. First, the Maikop thickness in the east was significantly greater than in the central and western Precaucasus [5]. This indicates that platform sediments were deposited mostly in the eastern sea. Second, the predominance of kaolinite over chlorite in the eastern section and its increase upward in section indicate active clay supply from the Platform. These clays included matter from eroded kaolinitic weathering products. The chlorite ratio increased in the Kuban' section, while more Caucasian detritus accumulated in the central Precaucasus. Third, the Sulak section was located in the vicinity of well-differentiated platform sediments. This is indicated by strong separation of geochemically nonmobile elements in the correlation diagram and the variation sequence. Concentration of nonmobile elements also increases slightly in the section.

Streamflow, shore erosion and eolian transport were the main agents to introduce sediments to the basin. The volume of sediment matter, introduced in the sea by eolian transport under a hot, humid climate that prevailed during a significant period in Maikop times was insignificant on this coast. The ratio of eolian matter that entered sediments was negligible. Even under more favorable conditions, such that exists presently on the Sea of Azov, eolian contribution does not exceed 10% in the sediments [25]. Shore erosion supplies approximately equal amounts of sediments along the entire basin periphery. In the absence of large-scale transgressive-regressive cycles, the ratio of abraded matter in the sediments was similarly insignificant.

Analysis of the mineralogical-geochemical depositional conditions of Maikop sediments, typical of the eastern and central Precaucasus, thus indicate accumulation mostly by sediment transport from the Russian Platform. They were fractionated in the Maikop paleobasin. Most of the terrigenous matter, derived from the Russian Platform accumulated in the northern part of the present Caspian Sea, off the mouth of a major Platform stream. This stream was comparable in size with the present Volga or Don Rivers. During late Maikop times, the flux of terrigenous matter from the Platform increased in the central Precaucasus area, while remained unchanged in the eastern region. This indicates a shift in the mouth positions of platform stream to the northern Stavropol' area. Postdepositional alteration in Maikop beds had a major influence on mineralogical geochemical sediment properties. Alteration impacted mostly the Sulak River section in which katagenetic clay illitization led to changed clay mineral ratios. The changes resulted in the significant redistribution of geochemically more mobile chemical elements. Redistribution of chemical elements was less intensive in the Kuban' River section in which diagenetic processes only were widespread. Apparently, sedimentary processes alone were responsible in defining clay mineral composition and clay mineral ratios.

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CHERT NODULES IN DEVONIAN AND CRETACEOUS CARBONATES ROCKS, BELARUS. ARTICLE 3: ORIGIN

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UDC 550.4:552.124.4:551.734(476)

A model is proposed for the formation and alteration of chert nodules in Devonian and Cretaceous carbonates of Belarus. The source of the silica for the nodules was the skeletal material of siliceous organisms. Chertification took place in conjunction with cementation, pressure displacement, entrainment, and replacement of carbonate sediments by silica, as well as an evolution of the silica along the line of opal-A → opal-CT → quartz. The modification of chert in the zone of groundwater infiltration is examined. Differences in the formation of chert in Devonian and Cretaceous deposits are described.

The stratigraphic position, distribution, occurrence, petrography, paleontology, mineralogy, and geochemistry of chert nodules in Devonian and Cretaceous carbonate deposits nodules of Belarus have been described in previous articles [9, 10]. In this paper we present a model for the environment and mechanism of deposition, as well as the subsequent alteration, of the chert.

INTERACTION OF CHERT AND SURROUNDING DEPOSITS, AND STAGE AND LITHOGENIC CONSTRAINTS ON CHERTIFICATION

Chert nodules in Cretaceous rocks of Belarus occur in subhorizontal layers, restricted to bedding planes (partings). This feature of the chert has been described in detail by Murav'ev [11] in many Cretaceous sections in the East-European platform. Moreover, using data from western Europe, Cyprus, and Israel, he correctly described the general aspects of the localization of chert in chalk beds.

It should be noted, however, that the arrangement of chert nodules in layers along bedding planes is also found in rocks of other composition and age. We have established this property in Devonian dolomites of Belarus; it has also been reported in bioclastic Albian limestones of the Upper Greensand of southern England, the Lower Carboniferous Ramp Creek Formation of southern Indiana [31], lower Turonian bryozoan limestones of Poland [34], and in many Precambrian carbonates [3].

Bedding planes are obviously related to periodic changes in the environment of sedimentation. These surfaces probably represent pauses in sedimentation, accompanied by some lithification of the sediment, as often shown in the Cretaceous by the presence of thin hardgrounds [2], "shell pavements," and numerous trails and burrows.

The cherts of Belarus contain many biogenic remains and traces of faunal activity. Devonian nodules contain gastropods, bivalves, nautiloids, brachiopods, sedentaria, stromatoporoids, corals, ostracodes, algae, and ichnites. All of the fossil material has been replaced by silica. The observations of A. M. Tsytenk, who established the presence of an exceptionally diminutive fauna in Devonian cherts [9], are important for determining the conditions under which silicification took place. He tended to associate this feature with rapid maturation (pedamorphosis). It is also possible that the geochemical environment leading to silicification had an inhibiting effect on growth, however.

Ichnites, as well as foraminifera, echinoderms, inoceramids, bryozoans, probable radiolarians, and siliceous sponges, are found in Cretaceous cherts. Unlike the Devonian cherts, carbonate shells have commonly not been silicified. Significantly, siliceous fossils are found that have been partially or completely replaced by carbonate.

Sulfides, partially or completely oxidized in the zone of meteoric water, are restricted to faunal remains in both Cretaceous and Devonian cherts.

Institute of Geology, Geochemistry, and Geophysics, Academy of Sciences of Belarus, Minsk. Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 55-68, November-December, 1993. Original article submitted April 20, 1992.

The abundance of fossils in Belarussian cherts is not accidental, and it is a key element in the development of a model for the formation of chert concretions. Many investigators have commented on the large number of fossils in chert nodules and on the restriction of chert to areas where body fossils and trace fossils are concentrated [1, 3, 32].

A study of the texture of Devonian and Cretaceous cherts of Belarus has shown that the nodules can be considered post-depositional, and represent the combination of two processes: 1) the replacement of carbonate material by silica, and 2) the growth of nodules by cementation and pressure displacement (forcing apart) of the bedding. Evidence of the first process and the post-sedimentational nature of the chert is the presence of silicified carbonate fossils and solution textures in the carbonate sediment. The second process is demonstrated by the absence of a reaction contact between the chert and the carbonate beds, by the presence (mainly in the Cretaceous) of dispersed carbonate material and considerable amounts of unaltered carbonate fossils in the chert, much of which is concentrated on the surface of the nodules, and by the nodular (rounded) form of the chert resulting from a tendency to a more favorable organization of the material, which is typical of "classic" concretions that form by growth from the center to the periphery by forcing apart the indurated sedimentary beds.

The data obtained indicate that replacement was more important, and cementation-forcing less, in the formation of Devonian chert nodules than in the Cretaceous cherts. In speaking of chert formation by replacement, it is important that we keep two different processes in mind [22]. This is a matter of "fast," i.e. metasomatic, and "delayed" replacement. Traces of the second type, represented by the nature of the cementation, are found in the chert in the form of silica fillings in solution pores in fossils that are more coarsely crystalline than the chert source.

In addition to the evidence noted above for the post-depositional nature of the chert we studied, we should also cite sulfide inclusions in the nodules, including clearly diagenetic concretions, the occurrence of silicate fossils replaced by carbonate that have survived chertification, and traces of early diagenetic cement in echinoderm encrustations. It is important to emphasize, moreover, that facies and paleogeographic control has been established for the distribution of $\delta^{18}\text{O}$ and the boron concentration in Cretaceous and Devonian cherts of Belarus. This characterizes the geochemical environment of the chert-forming basin and indicates that the process was diagenetic.

The conclusions we reached as to the stage and lithologic aspects of chert nodule formation, based on our studies of Belarussian cherts, are generally consistent with data from other regions. In summarizing a considerable body of published information [2, 6, 13, 18, 22, 31], the following conclusions were arrived at: 1) the formation of chert nodules begins no sooner than the stage of diagenesis (it is noteworthy that chert is not found in present-day oceanic carbonate sediments), and 2) different relationships are possible between the time of silicification and well known diagenetic reactions involving carbonates (precipitation of early cements, intergranular packing, transformation of aragonite and high-magnesian calcite).

Regarding our concept of a combination of methods of nodule formation, the overwhelming majority of investigators concentrate only on metasomatic replacement [1, 2, 17, 21, 23, 29, 38]. Only Hesse [22] and Maliva and Siever [32] consider a role for cementation.

SOURCE OF SILICA

It has been shown previously that Belarussian chert nodules were formed in a geochemical environment of aqueous ooze associated with sedimentation and, judging by the low concentrations of Ag, Pb, Cu, and other elements in the chert, beyond the influence of endogenic material. Although the concentration of silica in seawater during prediatom (pre-Cretaceous) time may have been higher than in modern seas, most investigators believe that ancient seas, at least during the Phanerozoic, were not saturated with respect to silica and that it was precipitated biogenically [4, 15, 18]. The concentration of silica in aqueous muds thus took place mainly by post-depositional solution of siliceous sponges, radiolarians, and during the Cretaceous, diatom frustules. This brings up two important questions: 1) how significant is the enrichment of pore waters by this means? and 2) is there a mass balance between skeletal and nodular silica?

According to Bernard [20], a study of a large number of deepwater samples from the Pacific and Atlantic oceans showed an average SiO_2 concentration in radiolarian and diatomaceous oozes of about 45 mg/liter, which is greater than the solubility of cristobalite (20-30 mg/liter) [39]. Levitan [6] has suggested that the precipitation of silica from aqueous muds in modern oceans is initiated at concentrations of more than 96-107 mg/liter, i.e. rather close to the equilibrium concentration of amorphous SiO_2 (60-130 mg/liter) [39]. It is important to keep in mind, however, that an estimate of the concentration of SiO_2 in ancient marine oozes, which could be appreciably greater, is difficult to arrive at on the basis of

data on the silica content in pore waters of modern oceanic sediments. Many types of flora and fauna (algae, echinoderms, etc.) are known to produce phenols that promote the formation of silica-chelating compounds of the diphenol complexes with catechol, as a result of which the solubility of SiO_2 is increased 700 times [24]. Meanwhile, investigators of modern oceans have concentrated mainly on deep-water zones, where material produced by organisms that promotes the formation of silica chelating compounds may not, for ecological reasons, be present. At the same time, in modern shallow marine carbonate depositional environments, which may be favorable for the occurrence of these organisms, there are no zones, as Knauth [29] points out, with an abundant silica biota.

We come now to the second question we posed, regarding the possibility of a biogenic source of the SiO_2 in the formation of chert, concerning the mass balance of chert and organic silica in ancient carbonate sediments. Although we have found no indications of siliceous organisms in Upper Devonian cherts of Belarus, there are traces of sponge spicules, sometimes quite abundant, in beds containing chert in the Glavno Devonian area, which includes the territory of Belarus [14]. As regards the Upper Cretaceous deposits, in addition to the sponge and radiolarians fossils we have shown to be present in the chert nodules, there are reports of spicules in the enclosing chalk and marl beds, sponges, radiolarians, silicoflagellates, and diatoms (20%) in upper Kontyakov tripolis and opokas, which are succeeded in the eastern part of the country by chalk, and there are interbeds of radiolarites and spongiolites of Late Cretaceous age in areas of Russia adjacent to Belarus [5, 12]. We note, moreover, that sponge, radiolarian, and diatom remains are typical of chalk beds [19, 22].

We can thus conclude that siliceous organisms occur in Devonian and Cretaceous basins containing chert-bearing deposits in Belarus. Were there sufficient resources of biogenic silica to form the chert nodules, however? This question has often been raised for other regions with regard to the lack of any positive correlation between these magnitudes in any carbonate sequences, including those we studied. There are two reasons for this discrepancy: firstly, the inadequacy of paleontological studies, as a result of which there are no observations of fossils of siliceous organisms, as pointed out by Shumenko and others [19]; secondly (and most importantly), intensive post-sedimentational solution of siliceous remains in conjunction with compaction of the sediment led to the total disappearance of traces of these organisms [6, 18, 31, 36].

The result is a paradox: the nature of the chert is not indicated by an abundance or even the presence of a siliceous fossil biota, while the presence of chert indicates the occurrence of siliceous organisms in the depositional basin. Often only indirect evidence of chert with a biogenic source is revealed: the restriction of chert to certain depositional environments that are favorable for siliceous organisms. But what are these environments? Do they include, for example, carbonate platform facies (shallow shelf) with Upper Devonian carbonates containing abundant benthonic fauna, bioherms, and biostromes, or epicontinental pelagic chalk facies? Maliva and Siever [31], analyzing a large amount of data on the distribution of chert nodules, conclude that the depositional environment of the chert-bearing rocks can vary, but nevertheless, chert tends to be found more often in subtidal limestone, below wave base, and is rare or absent in supratidal, intertidal, or high energy limestones and dolomites.

It is interesting that such amounts of organogenic silica can be preserved in carbonate rocks. If we take the typical thickness of a Cretaceous nodule horizon in Belarus (10 cm) and its spacing from the adjacent chert bed (50 cm), and assume that the SiO_2 that formed the horizon was mobilized from sediments above and below with a thickness two times half the distance between the chert beds, and correct for a 1.5 times thinning of the sediment by compaction [2], we find that the original sediment should have been composed of 10% skeletal silica.

The rhythmicity of the chert horizons in the carbonate section is related to periodic explosive growth of siliceous organisms. In a previous article [10] we showed that the distribution of $\delta^{18}\text{O}$ and the boron concentration in Devonian and Cretaceous cherts of Belarus reflected a global sedimentological event. Thus it is likely that the periodic bloom of silica biota was not of a regional character. Lisitsyn [7] reached the same conclusion regarding present-day and ancient chert formation in the oceans of the world, the waters of which contain silica from various sources. In this regard the increased concentration of SiO_2 in the water and, as a consequence, the bloom of siliceous organisms in the Devonian and Cretaceous basins, may have been caused by some very distant event. Such an event may have been an increased supply of SiO_2 from continental runoff [16], volcanism and hydrothermal activity [8, 11], or a zone of upwelling [13].

Evaluation of these factors in the increased concentration of soluble silica is a subject for separate study. We want to focus here on the close stratigraphic position of the chert-bearing Semiluk deposits of the Devonian Glavno area (including Belarus) and the highly silicified domanikoid (Rudkin) horizon of the Ural-Volga region. It does not appear as if chert formations are present in the Devonian of Belarus because of the introduction of silica by marine currents from the basins east of the East European platform, where domanikoids were enriched in silica by volcanic processes [8, 16].

One of the main questions in the origin of chert is what form the silica was precipitated in during the formation of the nodules in the oozes. Many cherts older than Late Cretaceous are quartzose, for example cherts in Upper Greensand carbonate rocks (K_1) and the Portland Limestone (J_3) in southern England, in the Ramp Creek beds, Onondaga Limestone (D_2), and Helderberg Formation (D_1) in the USA [31], and in the Upper Devonian rocks we studied in Belarus. Also, primary authigenic SiO_2 in deep marine oozes is usually opal-CT [41], and there are no oceanic pure quartz cherts without opal-CT younger than 40 million years [37]. Moreover, quartz cherts older than Late Cretaceous in the continental areas commonly contain lepispheres replaced by quartz and opal-CT cemented rinds [31], and Late Cretaceous and Paleocene cherts such as those in the Black Sea area [17, 19] and Belarus have minor amounts of tridymite and cristoballite. It thus appears that the quartz phase was preceded by opal-CT in the formation of chert.

But was opal-CT the first phase formed? A number of investigators believe that the initial form was a gel, i.e. amorphous SiO_2 [6, 11]. Actually, in the diagenetic sequence of siliceous oceanic sediments the phase of amorphous skeletal material (opal-A) and the first crystalline phase, opal-CT, a subdivision of opal-A phase represents a secondary nonbiogenic amorphous silica that began to precipitate immediately after burial of the skeletal material [39]. we have preliminary data, however, showing that some part of opal-A is composed of very fine crystals of opal-CT. Thus there appears to be some uncertainty as to which phase precipitates: amorphous or crystalline. This is related to the gradual transition of one phase into the other and dissolution of the boundary between them: the theory of colloidal systems suggests that the nuclei of elementary colloidal particles (micelles) are composed of dispersed matter and are represented by microcrystals or aggregates of microcrystals. One team of investigators of silica diagenesis has suggested therefore the possibility of precipitation of both an amorphous phase of SiO_2 (in systems with no impurities and at a $\text{pH} > 7$) and opal-CT as a result of flocculation of polymers with open structures (in systems with cations and a $\text{pH} < 7$) [40], and another proposed that amorphous SiO_2 films precipitated on organic layers of carbonate shells and that this gel phase later recrystallized to opal-CT [32].

Summing up, it is reasonable to suggest that, depending on the parameters of the ooze (concentration of the SiO_2 , salinity, etc.), in various areas the primary silica may precipitate both as rapidly recrystallized gel and as opal-CT. Later the silica may form quartz, not only following the more characteristic process of opal-CT $\rightarrow$ quartz but also possibly the transition opal-A $\rightarrow$ quartz [39] and direct replacement of carbonate material by quartz [30].

We now come to the question of specifically how chert formation takes place, what geochemical mechanism governs the migration and precipitation of silica to sediment. The framework of our model, which assumes that waters saturated with SiO_2 are formed from the dissolution of skeletal material, consists of several schemes touching on these aspects of the problem and is aimed at elucidating the conditions under which the carbonate substrate is replaced by silica.

Siever [38] has pointed out that the partial pressure of CO_2 in pore water is increased as a result of the oxidation of organic matter and, as a consequence, the pH is lowered, which can lead to an increase in the solubility of carbonate, a decrease in SiO_2 , and replacement of carbonate by silica. It is also considered likely that complex silica-organic compounds can form in areas where organic material has accumulated, creating a concentration gradient and bringing about the diffusion of SiO_2 solutions. This model is supported not only by the abundance of fossils in the chert, but also by the generation of microquartz crystals in the organic layers of brachiopod and pelecypod shells in ancient shelf deposits [23].

Since as a result of oxidation various materials appear, depending on depth of burial (first free oxygen, then manganese oxides, nitrates, iron oxides, and sulfates), the model specifies two variations. Holdaway and Clayton [23], considering that the other oxidation processes are associated with carbonate precipitation, which is unfavorable for silicification, assign free oxygen the principal role in the oxidation of organic matter, and point out that a certain amount of silica is precipitated before pyrite. Noble and van Stempvoort [36], on the other hand, consider sulfate reduction to be the main reaction bringing about silicification. Their basic arguments are: (1) in many cases free oxygen is depleted in the uppermost sediments; (2) pyritization is synchronous with the precipitation of SiO_2 or takes place earlier; and (3) there are experimental results that support bacterial sulfate reduction as a promoter of SiO_2 precipitation.

The chertification scheme involving oxidation of hydrogen sulfide was first demonstrated by Clayton [21] in the case of the unusual form of chert in Upper Cretaceous chalk deposits (England). This form, described early in the last century under the name of *paramoudra*, is a roughly cylindrical nodule with a chalk core containing pyritized trace fossils. Detailed study of these forms by Clayton established a singular interaction among the processes of pyritization, carbonate

cementation, and chertification in local areas of bioturbation; this formed the basis for a general model of chert nodule formation in chalk beds which, briefly, comes down to the following. A small amount of hydrogen sulfide (associated with a deficit of iron) is generated in the zone of bacterial sulfate reduction, part of which is used to form pyrite or marcasite while a large part migrates to the oxidation–reduction boundary zone in the sediment. Here the hydrogen sulfide is oxidized, lowering the pH, which produces differences in the solubility of carbonate and silica, leading to metasomatic formation of chert.

Using the "Dorag" model of dolomitization as a prototype, Knauth [29] proposed a scheme of chert nodule formation in coastal systems of mixed marine and meteoric water, where solutions are formed that are undersaturated with respect to calcite and aragonite and saturated (as a result of the leaching biogenic SiO_2 out of carbonate deposits by meteoric water) with respect to opal-CT and quartz. This is supported by the results of isotopic analysis of chert from various Phanerozoic deposits, which suggest that the meteoric component of the water affects the composition of the chert-forming solutions.

Maliva and Siever [32] noted the absence of corrosion of carbonate grains around the chert nodules, which may indicate undersaturation of the solutions with respect to carbonate. And since these investigators believe that chertification consists to a large extent of silica replacement of the carbonate substrate, they concluded that the nodule growth itself provoked an increase in the solubility of the carbonate. It was assumed that the growth of crystals of SiO_2 from saturated or supersaturated solutions brought about an increase in the pressure in thin films of the solution at the silica-carbonate contact, leading to a higher solubility of the carbonate. As a result the solution turned out to be unsaturated with respect to carbonate only in the contact zone. The volumetric rate of solution of carbonate and crystallization of SiO_2 were equal in this process, and beyond the replacement front the carbonate matrix might show no traces of solution. The question is raised as to how this process takes place in weakly lithified deposits, why there is no relaxation of the crystallization pressure of SiO_2 from the squeezing effect on the beds. Maliva and Siever respond to this question by considering the situation in the deep-water oceanic environment, where SiO_2 is precipitated early, before the metasomatic silicification front, in the form of cement [41], which creates a sort of rigid body within which replacement subsequently takes place in accordance with the mechanism proposed. The growth of chert thus includes simultaneous replacement of carbonate under the effect of force of crystallization within the nodule, isomineralic generation of SiO_2 crystals in a concentrically migrating outer rim, and interstitial cementation of the carbonate matrix at some distance from the nodule. Maliva and Siever ascribe the initial formation of the chert nodule to precipitation of SiO_2 on organic matter as a result of polymerization.

Our study did not include a detailed critical analysis of the foregoing genetic schemes, but it is useful for us to apply them to our study of chertification features in two specific basins in Belarus. The characteristic association with diagenetic sulfides shows that the process of chert formation in Devonian and Cretaceous deposits took place in a zone of sulfate reduction, i.e. where free oxygen supplies were exhausted. The scheme involving oxidation of organic matter is therefore inapplicable in our case. The establishment of a restriction of chertification to the reducing zone in sediments also casts serious doubt on the idea of SiO_2 precipitation at the oxidation–reduction boundary; in this case there would have to be either an uplift of the sequence of reducing sediment or subsidence of the redox boundary with the formation of each chert horizon, which considering the makeup of the geological section seems hardly likely. Moreover, the lowering of the pH during oxidation of H_2S should have produced a strong corrosive effect on carbonate grains in the sediment along the entire extent of the oxidation–reduction boundary, which has not been observed. Dissolution of carbonate deposits should have taken place everywhere around the chert nodules in the case of chertification associated with mixing of marine and meteoric waters. This concept, designed to explain the formation of chert in coastal regions, is also in poor agreement with the surprising stratigraphic persistence of the nodule horizons, which, for example, in middle Frasnian deposits, extend from the town of Vitebsk for several hundred kilometers westward. Moreover, this scheme of mixing of marine and meteoric waters does not explain the association of chert with fossils and sulfides. Therefore the replacement of carbonate by silica is apparently accomplished under the effects of bacterial oxidation of organic matter, sulfates in pore waters (sulfate reduction), and the development of pressures at the silica-carbonate contact by force of crystallization.

The general system of formation of chert nodules in carbonate deposits of Belarus takes place in the following manner (Fig. 1).

During periodically recurring intervals of Frasnian and Late Cretaceous age, related to geologic events that may have taken place far from the region under study, radical changes occurred in the study area in the hydrographic (mainly hydrochemical) marine environment leading to blooms of silica organisms. Changes in the ecology of the Frasnian sea in the corresponding time intervals are recognized by the appearance of a diminutive carbonate fauna.

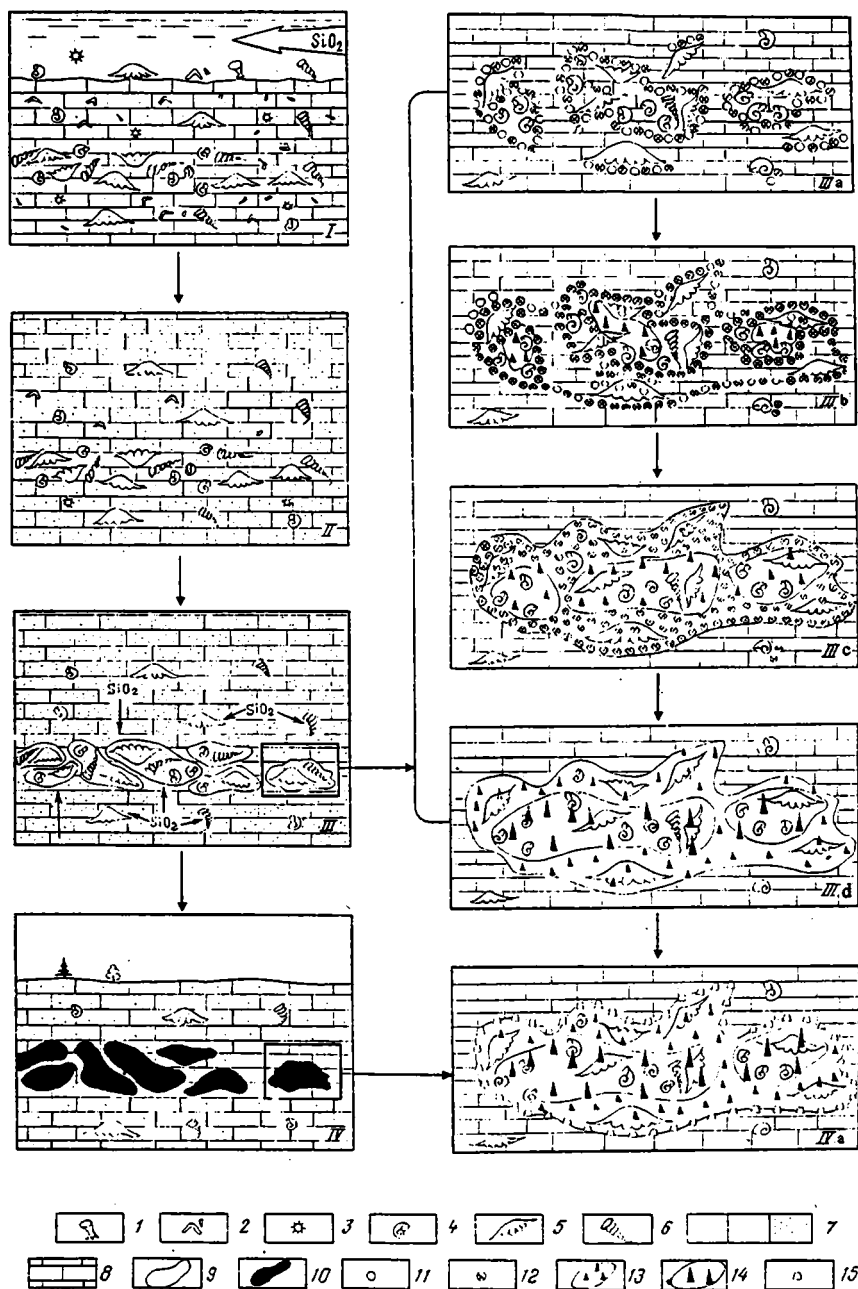


Fig. 1. System of formation and alteration of chert nodules in carbonate deposits. I) Marine currents introduce SiO_2 , a bloom of silica organisms sets in; II) the concentration of SiO_2 increases in the ooze as a result of the dissolution of siliceous skeletons; III) the pH decrease around shells in the zone of sulfate reduction leads to the deposition of SiO_2 , with a decrease in its concentration in solution and diffusion into those areas from surrounding sediment; IIIa) nodules take shape with cementation of the sediment with opal-A and opal-CT; IIIb) nodules continue to grow at the periphery, while internal carbonate is replaced by silica, which slowly recrystallizes; IIIc) nodule growth ceases, internal parts are altered: carbonate is completely replaced and opal-A is transformed into opal-CT; quartz area expands; IIId) further transformations take place: opal-CT is gone, the quartz core is more crystallized than the outer areas; IV) the nodule horizons enters the zone of meteoric water; IVa) a crust of marshallitized quartz is formed. 1) silica sponge; 2) sponge spicules; 3) radiolarians; 4) gastropods; 5) brachiopods; 6) foraminifera; 7) concentration of SiO_2 in aqueous solution, increasing from left to right; 8) carbonate substrate; 9) outline of forming chert nodule; 10) completely formed nodule; 11) opal-A; 12) opal-CT; 13-14) degree of crystallinity (13, less; 14, more); 15) marshallitized quartz.

Individual carbonate units are enriched in siliceous fossils, the diagenesis of which introduced silica into the ooze solutions. These solutions contained not only monomeric SiO_2 but also oligomers and larger polymers, i.e. were suspensions and sols [40].

Sediments enriched in silica solutions generally contain the remains of "carbonate fauna" and ichnites, which are concentrated at bedding surfaces.

The shift of these sediment systems out of the area of sulfate reduction led to oxidation of the soft tissues of buried organisms, which had not decomposed in the zone of free oxygen. This brought about the generation of CO_2 and H_2S , and as a result a decrease in the pH. On the one hand, this promoted the precipitation of silica from solution, mainly by destabilization of silica-chelating compounds [25], and on the other hand, an increase in the solubility of carbonates. Thus, the centers of the developing chert nodules were body fossils (gastropods, echinoderms, foraminifera, inoceramids, etc.) and burrows, and the fossils horizons were the future locations of nodule horizons.

The initial phase of silica, forming around fossils, was deposited in the form of intergranular cement, both forcing apart the beds and enclosing the carbonate substrate. As a result of the direct precipitation of opal-CT and its formation by crystallization of amorphous silica in pore spaces, a rigid framework of opal-CT was formed around the periphery, with a large amount of carbonate fragments inside. This formation of a sort of skeleton of the future chert nodule is attested by the absence of a reaction contact between the chert and the surrounding carbonate, as observed in modern deep marine sediments, indicating the formation of cement from lepispheres of opal-CT [41]. It is also supported by data from some continental sections, where spicules in the silicified zone have been shielded from compression, while in associated zones even nautiloid shells have been crushed [25].

At the same time as the framework of the nodule was being formed, two processes were taking place inside: (1) replacement of carbonate by silica under the effects of crystallization pressure formed at the contact of precipitating crystals of SiO_2 and carbonate grains, and (2) ripening (recrystallization) of silica inside of the nodule periphery. Replacement included both rapid and delayed types, which were expressed in the formation of pseudomorphs on one hand and a cementation texture on the other. The carbonate matrix could have been subject to replacement by both opal-CT and quartz [30]. The possibility, and intensity, of metasomatic replacement by the effects of force of crystallization was determined by not only the presence of a rigid cementational framework, but also the degree of lithification of the rocks. This is reflected in the far stronger metasomatism in cherts from well consolidated Devonian shelf dolomites than in weakly lithified Cretaceous pelagic deposits.

The ripening of silica was subject to Ostwald's law, relating to the solubility and morphology of the crystalline phase [30, 39], and includes the silica recrystallization path from opal-A through opal-CT (or directly) to quartz, with ever increasing degree of crystallinity. As a result, opal-CT was reduced to a minor amount in Cretaceous cherts, and quartz with an index of crystallinity of 0.6 was formed in the core of the nodules, as distinct from the surrounding area where the index was 0.4; Devonian cherts were completely devoid of opal-CT and the index crystallinity of the quartz was 4.3. It is curious that the index for Cretaceous cherts of Belarus is the same as for flints in shallow Cretaceous deposits of England [35], while the crystallinity typical of quartz in Devonian cherts is reached in Cretaceous deposits only upon burial to depths of 1500-3000 m in the central basin of the North Sea [26]. It cannot be not excluded, however, that this relationship does not result from thermobaric conditions at those times, as one might assume. It is quite likely that the initial phase of the silica differed in the Devonian and Cretaceous cherts: in the former, it was cristobalite-tridymite due to a high magnesium content of the substrate (dolomite) [27], while in the latter it was amorphous silica, which is shown by opal-A in the chert and the presence of a large number of shells that have been broken by shrinking of the gel.

ALTERATION IN THE ZONE OF METEORIC WATER

All of the samples of Devonian chert from Belarus have a white, earthy or mealy, highly porous crust or rind of various thicknesses, composed of marshallitized quartz. Among Cretaceous cherts, in addition to nodules without crusts there are cases of surface alteration which can be ranked according to intensity as follows: lighter than the main mass of chert, commonly with concentric shells run together → bluish-gray and porcelainous crusts → white earthy-mealy crusts.

Other investigators have reported the presence of crusts on chert [2, 17, 19, 31]. Some consideration has been given in these studies to the abundance of faunal remains and to the presence of tridymite and cristobalite, which commonly occur as lepispheres, and carbonate.

Some investigators [11, 30, 31] consider the crusts to be products of a reaction zone, in which accumulation, cementation, and replacement of the carbonate substrate has taken place. We do not deny the possibility of some such explanation for the external porcelainous border on chert nodules in deep-water oceanic deposits [41]. The crusts on the Devonian and Cretaceous cherts of Belarus, however, have long been removed from the zones of diagenesis and hydrodynamic infiltration (since Frasnian and Neogene times, respectively), and in our view are the products of aggressive effects of fresh meteoric solutions on the chert.

Although it seems quite apparent that solution of carbonates by alkaline waters probably stimulated the solution of silica, we have conducted a simple test under ambient conditions to confirm it (I. R. Tratsvetskaya, analyst). We used crushed chert, calcite powder, and bidistillate. The concentration of H_4SO_4 in solution for the system chert–water (1:5) after a week was 3.02 mg/liter, after 1.5 months was 4.93 mg/liter, and after 5 months was 23.70 mg/liter; for the system "chert–calcite–water" (1:0,1:5) it was 11.24, 13.80, and 31.52 mg/liter respectively. Mineralogical and petrographic study has yearly shown that the crusts are the result of marshallitization (breakdown) of the quartz, accompanied by a decrease in its index of crystallinity and loss of silica. The concentration of opal-CT and possibly opal-A in the crust, which is higher than in the interior of the nodule, is not a function of the younger age of this zone relative to the interior, as Maliva and Siever proposed [30], but to degradational transformation of the quartz phase under the effects of weakly alkaline water dissolving the carbonate rocks. This is confirmed by analysis of repeated sodium extracts from the chert, modelled after the natural process.

We have established a relationship between the degree of marshallitization of quartz, forming a crust, and the environment of chert in modern sections: in the zone of aeration, crusts are typically earthy to mealy and are composed of highly marshallitized quartz; in the zone of saturation, the crusts are dense and porcelainous and the quartz is less altered.

A connection between the breakdown of quartz and the effects of fresh water has been established in a number of areas. White clasts, formed during extensive weathering, are found among chert pebbles in Eocene and Neogene fluvial conglomerates of West Texas [33]. Transformation of dark quartzose chert into light Tripolilike rocks through a number of intermediate, highly porous, frothy chert varieties that typically contain a cristobalite phase has been established in unconformities in Late Cretaceous siliceous limestones of Jordan [28]. This example shows that aggressive infiltration of water can not only lead to breakdown of the peripheral parts of the nodules, but also completely alter the entire nodule. We have established this same effect, although not as strongly expressed, in Devonian cherts of Belarus, which provide a micropetrographic picture that is almost the same as for the crusts.

* * *

1. Nodular cherts in Devonian and Cretaceous Carbonates of Belarus are products of the mobilization of silica in oozes enriched in silica compounds as a result of the dissolution of the tests and skeletons of siliceous organisms.

2. The oxidation of organic matter of buried carbonate fauna in the sulfate reduction zone provided a geochemical environment favorable for precipitation of silica and dissolution of the carbonate substrate. The concentration of fossils (the seeds of chert nodule formation) at the bedding surfaces of dolomite and chalk predetermined the nodule horizons. Nodule formation was a combination of, on the one hand, cementation, forcing apart beds, and entrainment of material; and on the other hand, replacement of carbonate by silica.

3. Deposition of primary silica as quickly recrystallized gel and opal-CT in pore spaces was accompanied by forcing apart of the sediment and formation of a rigid nodule framework, in which fragments of the substrate were included.

4. During growth of the framework of the nodule at the periphery and after its cessation, fragments of carbonate sediment were replaced by opal-CT and quartz under the effects of crystallization pressure at the "silica–carbonate" contact and silica within the periphery ripened in the sequence opal-A → opal-CT → quartz. Upon formation of chert in weakly lithified deposits of chalk the role of cementation and forcing of the substrate was greater, and replacement less, than chertification in rapidly lithified Devonian shelf carbonates.

5. The introduction of the chert-bearing deposits into the zone of hydrodynamic infiltration zones brought about an aggressive effect on the chert by waters made alkaline as a result of the dissolution of carbonates in meteoric water, leading to marshallitization of quartz in the chert, which appears particularly apparent in the formation of external crusts on the nodules.

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PHYSICAL COMPOSITION OF DEPOSITS OF THE CALEDONIAN FRAMEWORK OF THE HANGAI SYNCLINORIUM (CENTRAL MONGOLIA)

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UDC 552.185:552.5(517.3)

Features of the mineral and chemical composition of the Vendian—Ordovician deposits of Hangai, represented by basaltoids, limestone, and basically terrigene rock, are considered. It is shown that the presence of association of basaltoids belonging to products of the volcanic activity of continental lithospheric platforms and sialic fragmented clastic will inverse correlation between the potassium—sodium ratios and silica observed in deposits from "fracture-type" basin attests to the primordial rifting nature of the Caledonian Paleolithic sedimentation basis of Hangai.

Thick monotonic terrigene Cambrian—Ordovician rock masses composed of sialic clastic are widely developed in the caledonides of Central Asia. These deposits are commonest within the Mongolian—Altai—Sayan region, where they have been studied in detail, particularly from the standpoint of lithology [4, 5, 7-12, 21, etc.]. In central Mongolia, coeval terrigene rock masses of similar composition and structure are responsible for the appearance of the caledonian framework of the Variscian Hangai-Haentei geosynclinal zone. The lithology of these rock masses have not been subjected to very intensive study. Special thematic investigations of these thick, uniform, primarily terrigene accumulations were carried by the present author in the late 1980s as part of a Joint Soviet—Mongolian Scientific Research Geological Expedition under the aegis of the USSR Academy of Sciences and the Academy of Sciences of the Mongolian Peoples Republic. In the present paper we will discuss the mineral composition of the Vendian—Ordovician deposits of Hangai, which is in the western part of the Hangai—Haentei geosynclinal zone.

VENDIAN—LOWER PALEOZOIC DEPOSITS OF HANGAI

Along the periphery of the Hangai synclinorium, or inner trough, which is filled with a Middle and Upper Paleozoic greywacke suite with intercalations of jasper and rare bands of volcanites of intermediate and acidic composition [19], Vendian-lower Paleozoic rock masses, including the Bayan-Hongor and Dzagin suites, are highly developed. It constitutes an independent structural formation that was formed in the course of Caledonian folding [3, 13].

The most representative sections of the Bayan-Hongor suite, and, in particular, the Dzagin suite, which is the principal subject of the lithological investigations, appear in western Hangai, in the basin of the upper and middle course of the Shara-Us-Gol River and its tributaries, where the width of outflow exceeds 60 km. Deposits that have become crumpled in a system of folds of different scales they are also nearly isoclinal, with predominant eastern dips, form the western margin of the synclinorium of the structure. From the Shara-Us-Gol section they may be traced to the east along the northeastern edge of the Bayan-Hongor zone, which exhibit dominant northern and north—northeastern dips. Accumulations of the Dzagin suite predominates in this band.

The Bayan-Hongor suite, which we studied in the basin of the Shar-Us-Gol River, consists of two rock masses, a lower volcanic—limestone terrigene rock mass (bh_1) with apparent thickness at least 1500 m, and an upper terrigene (bh_2) rock mass, up to 600-700 m in thickness (including the isoclinal folding). The base of the former rock mass (50-70% of the total thickness

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TABLE 1. Composition of Volcanites from the Bayan-Hongor Suite, wt. %

Component	Picrite-basalts		Basalts				Andesite-Basalts	
	4	20*	116u	137u	17	9a	117u	19g*
SiO ₂	45,89	46,32	47,43	47,63	49,94	50,31	52,20	53,05
TiO ₂	3,81	2,54	1,12	1,44	1,78	2,02	1,92	1,36
Al ₂ O ₃	11,32	13,40	18,92	13,66	12,14	14,70	14,21	19,78
Fe ₂ O ₃	6,36	10,78	7,21	5,86	5,70	6,40	9,54	2,97
FeO	9,78	8,35	3,85	7,22	6,79	6,26	3,42	4,03
MnO	0,24	0,20	0,06	0,26	0,26	0,10	0,04	0,10
MgO	7,21	7,88	10,53	8,26	6,61	6,17	6,20	3,89
CaO	7,57	1,37	1,20	8,42	8,51	6,29	2,76	3,69
Na ₂ O	3,17	3,87	0,86	3,17	4,27	2,10	2,36	3,67
K ₂ O	0,56	3,38	2,44	0,18	0,22	0,86	1,38	3,33
H ₂ O ⁺	4,22	3,25	5,28	3,00	2,90	3,91	3,73	3,25
H ₂ O ⁻	0,15	0,19	0,56	0,36	0,31	0,41	0,52	0,19
P ₂ O ₅	0,31	0,41	0,11	0,09	0,10	0,22	0,51	0,41
Fe ₂ O ₃ + FeO, at. %	0,55	0,56	0,36	0,46	0,50	0,52	0,52	0,49
Fe ₂ O ₃ + FeO + MgO								
Na ₂ O + K ₂ O	3,73	7,25	3,30	3,35	4,49	2,96	3,74	7,05
K ₂ O / Na ₂ O	0,18	0,87	2,84	0,06	0,05	0,41	0,58	0,92
MgO / CaO	0,95	5,75	8,79	0,98	0,78	0,98	1,38	1,05

Remark. Samples whose numbers include the letter "U" belong to the Vendian-Lower Cambrian deposits of the Underulan section (Chulut River). The analyses were performed at the Analytic Center of the Institute of Geology (Analysts: O. A. Burbaeva, N. L. Kalashnikova, M. V. Rudchenko, and E. V. Cherkasova).

*Analyses scaled on the basis of noncalcareousness (in both samples, CO₂ = 2.0 wt. %).

of the sections of the rock mass) consist of levels (100-350 m) of terrigene rocks formed of gray, dark gray, and black aleurolites, aleurolites, sandstone of different structures with intercalations and lenses of gritstones with "swimming" pebbles and fine- and intermediate-sized pebbled conglomerates with large dispersed pebbles and, rarely, boulders. In the lowermost strata of the rock mass, thin and finely fragmented material predominates, and in the uppermost strata, sandy and coarser clastic. The rate of schist formation also decreases in this direction.

The second most significant component of the lower rock mass (20-30% of the total thickness) is limestone, which form fine (1.5-2 m) and large (up to 50 m) lenses, as well as thick (250-300 m) and extended (50-60 km) stratified levels, each layer saturated with oncolites. The microphytolites which we have discovered in limestone from different stratigraphic levels data the Bayan-Hongor suite as Vendian to Early Cambrian [6]. Intercalations and lens (0.5 m to a few meters in thickness) of grayish-green aleurolite, black aleurolite, and phtanitoids, as well as limestone breccia and breccia conglomerate up to 3 m thick are developed among the limestone. Volcanites confined to the lower half of the rock mass are represented by levels (70-250 m) of basaltoids, sometimes accompanied by lava breccia.

The upper rock mass of the Bayan-Hongor suite is composed of terrigene formations with a broad granulometric spectrum, from conglomerates to argillite. The rocks are gray, dark gray, and black in color; greenish-gray, gray-green, and brownish (sideritized) varieties are also encountered. Sandstone of different compositions forming hands (10-55 m) with intercalations (up to 0.7 m thick) of alternating aleurolite and argillite predominate. The sandy packets are divided into sandy-gravelly conglomerate hands (5-6 m thick) or bands (at most 10 m thickness) consisting of a fine alternation of aleurolite and argillite containing strata (4-30 cm) of fine- and medium-grained sandstone, sometimes calcareous sandstone. Lenticular ore bodies of greenish-gray variolite are encountered in the rock mass.

In the course of a gradual transition, which we observed repeatedly, the Bayan-Hongor terrigene deposits ended up overlying the Dzagin suite. This transition is realized rather rapidly in the range 100-150 m by thickness and is expressed in the appearance, in the midst of grayish rock, of greenish-gray and green varieties, with the quantity and thickness of the intercalations of these rocks sharply increasing as we move upward in the section. The lower boundary of the Dzagin suite extends to the basement of the first level with a predominance of greenish deposits. Its age may be established from its stratigraphic position and encompasses the entire mid-Cambrian-Ordovician interval, or its mid-Cambrian-Early Ordovician

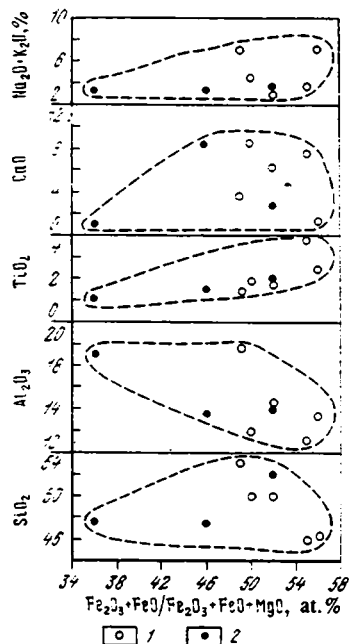


Fig. 1. Variational diagrams repressing basic-forming oxides as a function of the variation of ferruginosity: 1-2: sites of analyzed samples (1, basin of the Shar-Us-Gol River; 2, basin of the Chulut River).

part [6]. The Dzagin suite, whose observed thickness is more than 5 km, is subdivided into the following three rock masses (moving from below upwards): sandy-silt, sandstone, and pebbled sandstone, which are connected together by gradual transitions.

The lower fine- and thin-stratified rock mass (dz_1) is formed by greenish-gray, grayish-green, and green aleuropellite, aleurolite, and fine-grained sandstone with sharply conformable gray and brownish-gray varieties. The rocks are often schistose and have turned into chlorite – sericitic schist. In the uppermost strata of the rock mass rare seams of medium- and large-grained sandstone is encountered. Sills and dikes (up to 3 m thick) of diabase, plagioclasic porphyrite, and diorites are observed. The characteristic zones of the silification are 20-30 m wide, and the thickness of the rock mass varies from 700 to 1200 m.

The central, most representative part of the Dzagin suite (1.5-2 km thick) with rhythmic stratification is composed of green, gray, and move rarely, grayish-lilac colored, sandstone of varying compositions, from gravel to fine-grained. The thickness of the individual seams varies from 10 to 70 cm. They form hands from 10 to 45 m in thickness in which intercalations (a few centimeters thick) of aleurolite and both aleuropellite and packets (up to 1.5 m thick) consisting of a fine (from a few millimeters to 1-2 cm thick) interstratification of aleurolite, sandy aleurolite, more rarely aleuropellite, are observed. The sandy bands are separated by aleuropellite (from 3 to 25 m thick) containing low-thickness intercalations of medium- and fine-grained sandstone. The rock mass is broken up by fine bodies and dikes of diabases, rhyolite, and feldspar-quartz-prophyrite.

The upper predominantly grayish rock mass (dz_3) is formed of conglomerates, gritstone, and sandstone of different structures with subordinate bands (2-5 m) of alternating sandstone, aleurolite, and aleuropellite. Moving from below up in the section, the quantity and thickness of the intercalations and lenses of conglomerates increase gradually (from 10-15 cm to 1-2 m), with the maximum in the central part of the rock mass, where they form hands (15-25 m thick) containing intercalations and lenses (20-50 cm thick) of gritstone and sandstone. Amorphous proglyphs with traces of the vital activity of worms, are encountered at different levels. The observed thickness of the rock mass is 1000-1500 m.

Over the greater portion of Hangai there are tectonic contacts between the Dzagin suite and the superincumbent Devonian-Carboniferous deposits, moreover, in the northwest – southeast direction the latter are in increasing contact with its lower levels; in the region of the Dzag somon the thickness of the upper rock mass (dz_3) falls down to 500 m, and in the region of development of the Dzagin suite from the Dzhangalant somon to the Bayan-Hongor aimak, it is generally absent. Stratigraphic

relations between the Dzagin deposits and the younger rock masses are observed in the Shara-Us-Gol section, where the latter occur in the intermediate and upper rock masses of the Dzagin suite with aximuthal and angular displacement, sometimes together with basal conglomerates.

ROCKS OF BAYAN-HONGOR SUITE

Two categories of material — volcanic and sedimentary — participated in the formation of the Bayan-Hongor suite. The former is represented by lava, and the latter by carbonate matter and, principally, terrigene clastic; silica played a markedly subordinate role in the sedimentation process.

Volcanites belong to a weakly differentiated suite and, in terms of silica content, correspond to picrite-basalt, basalt, and andesite-basalt (Table 1).¹ The basaltoids are gray and greenish gray in color, sometimes lily-shaded. Aphyric varieties predominate; in the porphyry varieties, phenocrysts of plagioclase from different generations and, rarely, proxenes, are observed. The structures of the basic mass of the pilotaxitic and intersertal, more rarely, trachytoidal. The textures are compact; are fine (0.1-0.6 mm in diameter) amygdules filled with chlorite, quartz, and carbonate are characteristic.

The petrochemical features of the volcanites may be summarized as follows. In terms of content of alkaline content, depending on the silicic acidity [22], the greater portion of the basaltoids belongs to the alkaline suite, and the lesser portion, to the tholeiites. An increase in ferruginosity is accompanied generally by accumulation of silica, alkalis, titanium, and calcium (Fig. 1). High titanium oxide contents ($\bar{x} = 2.0$ wt. % for relatively low values of P_2O_5 , $x = 0.27$ wt. %). In terms of the nature of the differentiation and content of the basic petrogenic components, the Bayan-Hongor volcanites are comparable to products of the volcanic activity of the continental lithospheric platforms, in particular, rift-forming zones.

The distinctive geochemical feature of the basaltoids is the fact that they are depleted of nickel (Table 2); the mean value of the N/Co ratio is at most 1.5. This is apparently due to the fact that they are the products of low-depth differentiation of mantle magmas in intermediate vents [14], which are characteristic of mature rifts. The samples that have been analyzed were taken from the upper strata of the lower rock mass of the Bayan-Hongor series; no lower stratigraphic contacts whatsoever with ancient deposits are observed in this region.

The basaltoids exhibit substantial variations in titanium and zirconium contents; their ratios range from 112 to 287 ($x = 173$). There is a clear direct correlation between these elements; in the TiO_2 —Zr diagram the field of volcanites is parallel to the titanium and zirconium correlation line for nondepleted mantle [23].

In the Bayan-Hongor deposits, which developed to the south of the somon Gurvan—Bulak, a breccia level is encountered; the base of the level consists of highly blistered modified vitreous fragments that had been transformed into a quartz-albite-chloritic aggregate containing rare laths and fine phenocrysts of saussuritized plagioclase. Fragments of glass of the dimensions of sand and gravel are characterized by a heterogeneous configuration; some of them are lenticular in form with a subparallel orientation of the continuous amygdules. The fragmented structure of the vitreous mass is missing in places, and it assumes a lava-like appearance with elements of fluidization emphasized by the "laminated" distribution of the mineralized leucoxenize matter. Gravely angular and rounded-angular fragments of brownish basalts are scattered in the groundmass together with hyalopilitic, hyaloophitic, and pilotaxitic structures and typical lava formations of the Bayan-Hongor suite.

Formally speaking, this type of rock may be defined as pillow hyalobreccia [20], though it appears to possess a different mechanism of formation. This is attested to by such data as the absence of associated pillow lava, frequent development of lava fluidal sections and transition into hyalobreccia, and the presence of lenticular fragments together with continuous subparallel oriented blisters that had been transformed in the course of deposition. Such structural features are probably attributable to the specific nature of the outflows of highly gas-saturated lava in the shallow sea environment accompanied by gushing; basalt fragments were formed not as a result of rupture of the pillows, as occurs in pillow hyalobreccia, but were captured by moving magma. Therefore, we defined these rocks to be lava-breccia.

Limestone are present in varieties that are white, different shades of gray, up through dark varieties, more rarely, rose-colored, and contain microphytolites (organic) or are lacking in microphytolites. Nonrecrystallized varieties are finely or closely crystallized, and the organic residues are composed of crypto- and fine-grained carbonates; in the microphytolitic limestone from the Vendian part of the section, we observed an inverse relation between the grain size of the groundmass and

¹The fact that the analytic material is not representative is principally because of the frequent carbonization of the volcanites cause by the high CO_2 content.

TABLE 2. Contents of Minor Elements in the Basaltoids of the Bayan-Hongor Suite, g/ton

Element	Picrite-basalts		Basalts				Andesite-Basalts	
	4	20	116Y	137Y	17	19a	117u	19g
Data of X-ray Analysis								
Rb	<10	14	78	<10	<10	16	42	87
Sr	230	44	63	220	140	180	120	790
Y	25	43	10	16	33	29	25	10
Zr	190	130	39	65	100	180	110	99
Nb	19	13	<10	<10	10	<10	<10	<10
Ba	140	120	600	<10	100	210	270	910
La	<10	<10	<10	<10	<15	<15	<10	34
Ce	34	<10	<10	<10	<15	33	29	62
Data of Spectroscopic Analysis								
Cr	135	50	140	70	55	95	8	8
Ni	48	38	53	40	40	65	19	20
V	200	350	190	195	250	200	200	190
Cu	43	60	50	85	50	60	90	38
Zn	110	85	55	53	80	85	85	85
Co	37	24	26	29	27	32	22	18
Pb	5	5	7	5	<5	9	10	19
Ga	25	20	19	14	16	25	20	27
Ge	<1	≈0,9	≈0,9	<1	1,4	≈0,9	1	≈0,9
Mo	<1	<1	1,2	1	<1	<1	1,4	<1

the organic residues, moreover, the central part of the oncolites are finely crystallized, and along the periphery fine-grained carbonate has developed. The limestone is marmorized and highly fractured; the fractures are filled with fine- and medium-grained calcite and dolomite. Numerous pyritic crystals are often scattered in the gray and dark limestone. The rose color of the limestone is attributable to iron hydroxide confined to small fractures and pores; cold-like elements are observed in these types of limestone, as is emphasized by silicification and (or) ferrous films.

The CaCO_3 content in the limestone varies from 90 to 98%, that the MgCO_3 does not exceed 1%, and the insoluble residue amounts to 0.7-8%; under the microscope muscovite-type mica flakes and quartz silt may be recognized. There are varieties of Vendian oncolitic limestone in which the CaCO_3 content does not exceed 50%, that of MgCO_3 grows to 39%, and the insoluble residue is more than 11%. In terms of the composition of components these rocks correspond to dolomites, through, microscopically, they do not differ from marmorized oncolitic limestone except for the fact that relatively large rhombohedral dolomite is observed in the fractures.

The silicite belongs to formations of the phthanite series. They are in the form of gray, dark grayish, and black crypto- and micrograined pyrite-impregnated quartz rocks containing various quantities of hydromica flakes and fine chlorite isolations as well as numerous quartz and quartz-chlorite veins. The phthanitoids form finely and closely stratified (thickness of the individual strata up to 20 cm) low-thickness (0.6-0.7 m) intercalations that are spatially connected to the limestone and occur mainly in the rift-forming block or within it. Moreover, in the latter case black silicium alternates with black and dark gray shale of comparable thickness (0.5-0.7 m), the thickness of these bands reaching 3 m.

Light gray and bluish-gray microquartzite, constituting an intergrowth of micro- and fine-grained quartz, hydromica, and chlorite, are encountered among the terrigenous rocks. The rocks are highly fractured and small sections of black crypto-grained phthanitoids, which represent evidence of the primordially siliceous nature of the microquartzite, are preserved along certain veins; moreover, intercalations containing recrystallized radiolariae sometimes occur in the latter; diagenetic pyrite crystals nearly completely filled with substituted ferric oxide, are observed.

data of chemical analyses of the silicite and microquartzite are presented in Table 3.

The terrigenous rocks determine the outward appearance of the Bayan-Hongor suite; the dimensions of the material forming these rocks varies greatly, from boulders down to pelites. Sandstone of different structures markedly predominates. The rocks are gray, dark gray to greenish-gray in color, with lilac-rose varieties are sometimes observed, the color of the latter attributable to layered sideritization of different intensities. In terms of the content of the basic rock-forming components (Q, F, and R), all the fragmental rocks, with rare exceptions, belong to the mictic group, the percentage of each being less than

TABLE 3. Composition of Siliceous Rock of the Bayan-Hongor Suite, wt. %

Rock	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO
Silicate	90,01	1,63	1,59	2,16	0,04	1,32
"	93,01	0,57	1,99	1,71	0,04	0,80
Microquartzite	93,24	1,10	1,58	0,89	Her	0,42

Rock	CaO	Na ₂ O	K ₂ O	H ₂ O ⁻	H ₂ O ⁺	P ₂ O ₅
Silicate	0,47	0,19	0,57	0,12	1,51	0,004
"	0,68	0,19	0,35	0,06	0,11	None
Microquartzite	0,47	0,42	0,82	0,17	0,43	"

Remark. 1. The determinations were performed at the Analytic Center of the Institute of Geology (Analyst: O. A. Burbaeva). 2. TiO₂, CO₂, and C were not detected.

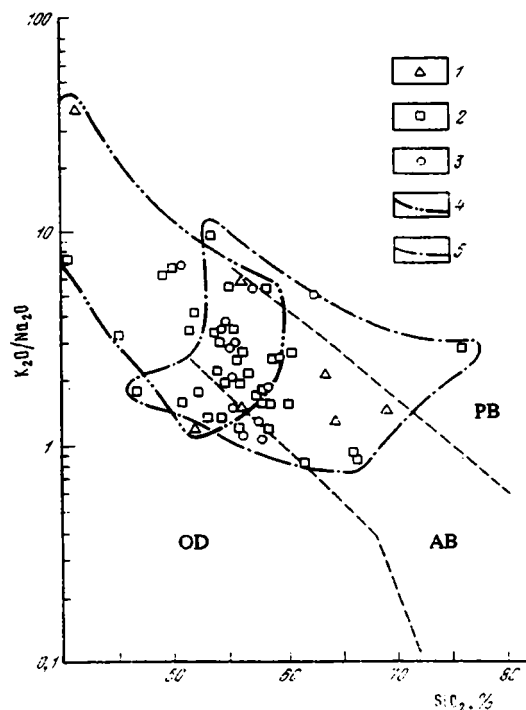


Fig. 2. K₂O/Na₂O-SiO₂ variational diagram for argillite and aleuropelite in Hangai. (1) Bayan-Hongor suite; (2) and (3) Dzagin suite (2, lower and intermediate rock mass; 3, upper rock mass); (4) and (5), boundaries of fields (4, argillite; 5, aleuropelite). The broken lines show the boundaries of the different tectonic environments [23]; PB, passive border; AB, active continental border; OD, oceanic island arc.

50%. Three types of rocks may be distinguished on the basis of the relative predominance of a particular component in this group: first, feldspar-quartz-lithic (the most widespread rock), lithofeldspar-quartz (less highly developed), and feldspar-lithoquartz rock, which occurs episodically.

The overwhelming proportion of the lithic fragments belong to two categories of material, magmatic or metamorphogenic. In the first group, which often is dominant in the coarse-grained rock, are found coarse-crystalline granitoids, including granite (sometimes with muscovite), aplite (isolated), veined quartzite (occasionally with epidote); the second group, which is most characteristic of the medium- and fine-grained rocks, includes heterogeneous shale; quartz-muscovite, micaceous- and quartz-chlorite, quartz- and muscovite-biotite, chlorite-sericite-biotite, chlorite, and carboniferous

TABLE 4. Composition of Fine-Grained Rocks of the Caledonian Framework of Hangai, wt. %

Component	Bayan-Khongor Suite (bh)			Dzagin Suite (dz ₁₊₂)			Dzagin Suite (dz ₃)	
	schist (2)	argilite (2)	aleuopelite (2)	schist (4)	argilite (7)	aleropelite (20)	argilite (7)	aleuopelite (9)
SiO ₂	$\frac{46,65}{55,86}$	$\frac{59,81}{29,5}$	$\frac{62,71}{84,5}$	$\frac{48,71}{49,92}$	$\frac{55,16}{36,69}$	$\frac{56,69}{31,42}$	$\frac{54,9}{4,22}$	$\frac{57,76}{4,18}$
TiO ₂	$\frac{1,43}{0}$	$\frac{1,13}{0,002}$	$\frac{0,82}{0,05}$	$\frac{1,27}{0,06}$	$\frac{1,26}{0,24}$	$\frac{1,06}{0,065}$	$\frac{6,58}{0,07}$	$\frac{1,14}{0,09}$
Al ₂ O ₃	$\frac{23,44}{7,68}$	$\frac{14,74}{12,4}$	$\frac{12,7}{1,25}$	$\frac{21,98}{16,72}$	$\frac{17,65}{11,99}$	$\frac{18,00}{7,54}$	$\frac{18,89}{1,94}$	$\frac{16,87}{3,02}$
Fe ₂ O ₃	$\frac{3,62}{2,7}$	$\frac{5,68}{0,67}$	$\frac{2,72}{0,2}$	$\frac{4,33}{1,9}$	$\frac{5,85}{12,67}$	$\frac{3,63}{2,71}$	$\frac{3,8}{4,24}$	$\frac{2,98}{3,17}$
FeO	$\frac{6,07}{0,54}$	$\frac{4,39}{0,65}$	$\frac{4,28}{1,26}$	$\frac{5,95}{0,61}$	$\frac{4,00}{3,38}$	$\frac{4,63}{1,8}$	$\frac{5,16}{0,56}$	$\frac{5,02}{2,05}$
MnO	$\frac{0,075}{0,005}$	$\frac{0,03}{0,001}$	$\frac{0,045}{0,00005}$	$\frac{0,06}{0,0008}$	$\frac{0,03(4)}{0,03}$	$\frac{0,06}{0,001}$	$\frac{0,04}{0,001}$	$\frac{0,06}{0,0004}$
MgO	$\frac{5,29}{1,76}$	$\frac{4,03}{1,06}$	$\frac{3,68}{0,79}$	$\frac{5,6}{2,78}$	$\frac{4,82}{0,73}$	$\frac{4,53}{2,34}$	$\frac{4,8}{0,38}$	$\frac{4,33}{0,45}$

CaO	$\frac{1,48}{0,05}$	$\frac{1,10}{0,52}$	$\frac{3,03}{10,03}$	$\frac{1,32}{0,02}$	$\frac{1,66}{3,9}$	$\frac{1,41}{0,3}$	$\frac{1,19}{0,31}$	$\frac{1,43}{0,25}$
Na ₂ O	$\frac{1,54}{3,59}$	$\frac{0,95}{0,15}$	$\frac{1,80}{0,045}$	$\frac{1,4}{0,16}$	$\frac{1,21}{0,41}$	$\frac{1,71}{0,42}$	$\frac{1,3}{0,35}$	$\frac{1,84}{0,25}$
K ₂ O	$\frac{5,34}{6,7}$	$\frac{3,24}{0,77}$	$\frac{2,68}{0,115}$	$\frac{4,65}{2,25}$	$\frac{3,8}{0,82}$	$\frac{3,55}{0,64}$	$\frac{3,74}{0,64}$	$\frac{3,77}{0,53}$
P ₂ O ₅	$\frac{0,195}{0,006}$	$\frac{0,04}{0,0001}$	$\frac{0,195}{0,00005}$	$\frac{0,17}{0,02}$	$\frac{0,12}{0,0014}$	$\frac{0,12}{0,0038}$	$\frac{0,13}{0,016}$	$\frac{0,105}{0,02}$
FeO*	$\frac{10,05}{6,5}$	$\frac{10,63}{0,007}$	$\frac{7,28}{0,58}$	$\frac{10,71}{1,59}$	$\frac{10,44}{4,8}$	$\frac{8,62}{1,77}$	$\frac{9,34}{2,85}$	$\frac{8,3}{1,11}$
FeO / MgO	$\frac{1,9}{0}$	$\frac{2,73}{0,52}$	$\frac{1,9}{0,06}$	$\frac{1,91}{0,43}$	$\frac{2,16}{2,63}$	$\frac{1,9}{0,58}$	$\frac{1,95}{0,3}$	$\frac{1,92}{0,19}$
K ₂ O / Na ₂ O	$\frac{1,22}{37,74}$	$\frac{3,95}{6,56}$	$\frac{1,49}{0,0002}$	$\frac{3,32}{6,66}$	$\frac{3,14}{5,94}$	$\frac{2,08}{4,0}$	$\frac{2,88}{3,44}$	$\frac{2,05}{2,87}$
SiO ₂ / Al ₂ O ₃	$\frac{2,02}{0,3}$	$\frac{4,22}{1,88}$	$\frac{4,99}{1,34}$	$\frac{2,22}{0,62}$	$\frac{3,12}{1,01}$	$\frac{2,9}{1,74}$	$\frac{2,9}{0,06}$	$\frac{3,42}{0,27}$

Remark. 1. The arithmetic mean (x) is given in the numerator, and the standard deviation (S) in the denominator, while in parentheses, the number of specimens analyzed.

2. FeO* is the total quantity of iron scaled as ferrous iron.

3. The analysis were performed at the Analytic Center of the Institute of Geology (Analysts: O. A. Burbaeva, S. N. Gordeeva, N. L. Kalashnikova, V. V. Karpushina, M. V. Rudchenko, and E. V. Cherkasova).

TABLE 5. Content of Minor Elements in Fine-Grained Rocks of the Caledonian Framework of Hangai, wt. %

Element	Bayan-Khongor Suite (bh)			Dzagin Suite (dz ₁₊₂)			Dzagin Suite (dz ₃)		Clarks of Sedimentary Rocks (clay and schist) [17]
	schist (2)	argillite (2)	aleuropelite (2)	schist (4)	argillite (7)	aleuropelite (20)	argillite (7)	aleuropelite (9)	
Date of X-Ray Analysis									
Zn	99	99	70	119	95	99	92	98	80
Rb	160	120	83	155	140	120	138	132	200
Sr	61	26	118	78	44	67	63	79	450
Y	32	22	21	27	20	23	22	23	30
Zr	180	130	135	157	127	145	128	142	200
Nb	12	11	14	14	12	12	13	14	20
Ba	1065	1720	520	847	687	755	753	820	800
La	32	29	32	37	30	30	26	33	40
Ce	72	52	52	71	54	60	52	62	50
Data of Spectroscopic Analysis									
Cr	135(1)	87(1)		88(2)	100(7)	96(4)	92	100	
Ni	68	40		50	49	48	42	95	
V	268	155		147	169	152	155	130	
Cu	68	48		33	52	42	44	57	
Co	20	8		17	17	13	14	20	
Pb	17	4		11	16	9	19	20	
Ga	26	16		17	19	18	17	30	
Ge	<1,5	<1,5		1,7	2,1	1,9	2	2	
Mo	<1,5	<1,5		<1,5:2	<1,5	<1,5	<1,5	2	

Remark. The number of analyzed specimens is given in parentheses.

rocks; microquartzite (sometimes ferric microquartzite) is present in lesser quantities, and may contain flakes of muscovite and small rhombs of siderite and marmorized limestone, occasionally chlorite-epidote-plagioclase gneiss. Fragments of sedimentary rocks, such as argillite, aleuropelite, mica-quartz-aleuropelite, silicite, as well as variolite are encountered sporadically. Rocks that form the upper strata of the terrigenous rock mass are characterized by fragments of pegmatite and granitoids with highly pelitized and sericitized fragments (metasomatite of feldspar and rock fragments).

The quartz is primarily grainitoid, both monogranoblastic and monocrystalline, the latter usually fractured, the fractures overlain by a black leucoxene-type ore matter, in the form of thin inclusions of granitoid fragments in the quartz. Postsedimentary fractures in the fragmental quartz are filled with calcite, more rarely chlorite together with calcite. The feldspar rocks are heterogeneous and are represented by both potassic and limestone-sodic varieties. Orthoclase, often with ingrowths of plagioclase (perthite), is most typical; microcline with typical microclinal lattice is encountered. There are both weakly modified acidic plagioclase rocks as well as rocks that are sericitized to different degrees, right through complete substitution, though in this case they are recognized from the crystal habit of the mineral. Feldspar injected with quartz (micropegmatite) occurs.

Muscovite is typical, its content being highly variable; it is rare in the coarse-arenaceous rock and is represented there by coarse plates, with greater quantities present in aleurolite and fine-arenaceous varieties. Strongly weathered biotite and fine lenticular inclusions of organic matter occur sporadically. The most commonly occurring accessory minerals are magnetite, hematite, ilmenite, and apatite, with zirconium, blue-green tourmaline, epidote, and sphene being less widespread; isolated grains of light green granate also occur. Large diagenetic crystals of partially or completely oxidized pyrite are sometimes encountered.

Grading of material is either absent or very weak; the fragments are semirounded; orthomorphism and incorporation are observed, and as a result the mica and soft schist and argillitic fragments are usually deformed and lenticularly elongated. The cement is filmy, of secondary chlorite-hydromicaceous, or quartz-chlorite-hydromicaceous type, and is sometimes carbonated.

Besides the mictic formations rocks from the lithic group in which the content of rock fragments exceeds 50% are encountered. These include certain types of gritstone composed of granitoids, quartzite, mica schist, chloritized fragments, epidosite, and quartz-epidotic metasomatites; granitoid quartz, orthoclase, pertite, microcline, and plagioclase are present in them. The binder mass consists of aleuritic fine- and medium-grained sandstone of the same composition together with fragments of muscovite. The cement is of a filmy, hydromica-chlorite-carbonate type. Uneven carbonatization and sideritization are sometimes observed.

Terrigene fine-grained rocks are represented by aleuropelite and argillite, sometimes transformed into schist. There are very few purely clayey varieties, with aleurite of quartz, feldspar, muscovite, chlorite-sericitic schist, apatite, and organic detritus usually present in the fine quartz-chlorite-hyromicaceous groundmass; if the quantity of the aleurite reaches 30-50% of the total volume of the rock, it is defined to be aleuropelite. In the schist-argillite-aleuropelite petrochemical series, an increase in the quantity of silica with decreasing titanium, aluminum, magnesium, and potassium content (Table 4) is observed. By comparison with schist and clay clarks, in the earth's crust rocks are enriched with titanium (by a factor of 1.5-2.5). The quantity of manganese is below that of clark, while the quantity of manganese is below that of clark, while the quantity of phosphorus in the schist and aleuropelite is above that of the clark level by 100 g/ton. the mean values of most of the microelements is at the clark level or below; low contents of nickel and very low contents of strontium and high contents of vanadium and barium, and, in the schist, of cerium, are characteristic (Table 5).

ROCKS OF THE DZAGIN SUITE

The Dzagin suite is a thick monotone terrigene rock complex without reference horizons and composed exclusively of terrigene material of a broad granulometric range, from clay to boulders, the proportion of coarse clastic generally increasing through the section from bottom upwards.

In terms of mineralogical composition, the fragmental rocks are similar to the Bayan-Hongor suite, though formations of the quartz group are dominant here; the proportion of quartz in these formations is 50% and more, that of feldspar 25-30%, while the lithic fragments are responsible for at most 20% of the total volume of the fragments. These rocks are determined as feldspar-quartz. They gradually (within the lower rock mass of the Dzagin suite) supplant the mictic group formations which are characteristic of the Bayan-Hongor suite. The other mineralogical feature of the Dzagin rocks is the sparse collection of lithic fragments. Granitoids, aplites, and veined and metamorphosed quartzite are always present; the latter often contain different quantities of subparallel oriented muscovite-type mica, and sometimes amphibole. In the arenaceous fraction the quantity of "soft" rock is sharply reduced; there are isolated fragments of micaceous and muscovite-chlorite schist, quartz aleurolite, aleuropelite, and marmorized limestone. The groundmass of the schist falls within the silt fraction, probably because of their disintegration in the course of sedimentation.

The gritstone and conglomerates have the same mineralogical composition as the sandstone, though with different quantitative relations between the rock-forming components; lithic fragments predominate, with quartz and feldspar subordinate. These rocks are determined as quartz-lithic.

On the whole, in terms of mineralogical composition the Dzagin fragmental rocks are more mature than rocks from the Bayan-Hongor suite, attributable to redeposition of material from the same distributive province in the sedimentation process, which led to dwarfing of the "soft" schistose fragments. At the same time, the subjacent rock was subjected to a process of rewashing, which led to be presence in the base of many grade-sorted strata of fragments of argillites and aleuropelites of a coarser size than the basic mass of the deposit. Moreover, fragments of silicites containing spicules of siliceous sponges appear, pointing to erosion of the Paleozoic (Cambrian) deposits [16, 18].

Substantial differences in the formations of the two terrigene suites we have been comparing are found at the structural level. A profuse clay-silt matrix (up to 30%, and in the fine- and medium-grained sandstone, up to 50% of the total volume of rock) containing, besides quartz and feldspar, numerous fragments of mica-chlorite and chlorite schist, are inherent to the Dzagin sandstone, gravel, and pebbled accumulations. They are basically diamictic varieties, e.g., sandstone, gravel, and pebble. Another characteristic feature of the structures lies in the subparallel orientation of the plates of mica, schist, and argillite fragments, and elongated grains of quartz and feldspar. The phenomenon is one of sedimentation, caused by an autokinetic mechanisms of transport of fragmental material, at the same time as analogous structures observed in the Bayan-Hongor suite (and in the lower strata of the Dzagin suite) are generally post-sedimentation in nature and attributable to processes of schist formation and metamorphism.

An abundance of clayey hydromica-chlorite material is inherent to aleurolite; dispersed organic detritus and decomposed biotite are encountered; there is considerable amounts of magnetite in some of the varieties.

The terrigene fine-grained rocks include aleuropelite and argillite which are mineralogically similar to the Bayan-Hongor suite, though here organic detritus is encountered only sporadically and in small quantities. They are less siliceous and more aluminiferous (cf. Table 4), whence the values of the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio is also lower (3 versus 4-5 in the Bayan-Hongor rocks); moreover, they are less ferruginous, but more manganous, though on the whole they exhibit the same trend of iron enrichment (greater by a factor of 2-2.5 by comparison with clark) and manganese impoverishment (lesser by a factor of 1.5-2 by comparison with clark). The content of the remaining petrogenic components is roughly at the same level as in the argillite and aleuropelite rocks of the Bayan-Hongor suite. This situation extends as well to the microelements, except for barium and vanadium, the quantity of which is lower and approaches that of clark.

PHYSICAL COMPOSITION AS AN INDICATOR OF THE DISTRIBUTIVE PROVINCE AND TECTONIC ENVIRONMENT

Terrigene sedimentation was dominant through Hangai during the Vendian-Ordovician era. The composition of the fragmental material and its quantitative relations reflect the distinctive features of the structure of the distributive province, which consists of metamorphites represented by heterogeneous forms of schist, quartzite, including ferruginous quartzite, marmorized limestone, and gneiss. Judging from the abundance of acidic volcanites, they burst through in the form of thick bodies of coarse-crystalline granitoides and granites accompanied by heterogeneous veined facies.

The distribution of the psephytic facies and certain tectural features of the terrigene accumulations (pillow marks of current ripples and elements of cross bedding) underscores the principal source of the clastic, which is situated to the west and southwest of the contemporary outcrops of the terrigene suites we are considering, within the Central Mongolian massif. An Achean-lower Proterozoic basement consisting of tonalite gneiss, migmatite, amphibolite, marble, and quartzite, sometimes ferruginous, and a low- and medium-Riphean green-schist complex may be distinguished in the structure of the massif. Here cupola structures formed of medium- and coarse-crystalline granitoids represented by quartz diorite, tonalite, and plagiogranite, have also developed. Within these rocks we may also find acidic plagioclase, quartz, hornblende, and biotite, with orthoclase (3-8%) present in the plagiogranite; sphere, apatite, zirconium, magnetite, and pyrite are characteristic accessory minerals. Rose colored potassium granite present here and composed of plagioclase, microcline, quartz, biotite, and muskovite, belong to the pre-Late Riphean intrusions [2].

Rift-forming troughs running in a northwest strike [1, 15] in which the terrigene-volcanogenic complexes have accumulated, are embedded in the latter reef in the body of the Central Mongolian massif. In the Vendian era the western border of the massif developed as an active Pacific-Ocean type continental border [2]; at this time the eastern edge of the ancient continent underwent processes of extension, forming the Shara-Us-Gol rifting structure that runs in a northwest strike with a characteristic association of volcanites corresponding to intraplatform basalts together with terrigene syalic material.

In recent decades there have been studies published that focus on the relation between the composition of fragmental rocks and the tectonic environment under which they formed. These studies have considered both the mineral composition of the sands and sandstone, as well as the geochemical features of the sand and sandstone, mainly through the application of the quantitative characteristics of the potassium-sodium ratios and silica. Many of these studies have been discussed in an article by B. Rosen and R. J. Korsch [24], which not only reviewed the values of the parameters in the fragmental formations, but also extended them to clay the argillite. in the $\text{K}_2\text{O}/\text{N}_2\text{O}-\text{SiO}_2$ diagram they distinguished three fields corresponding to tectonic categories passive and active continental borders and ocean island arc.

In this variational diagram, the specimens of the terregen suites of Hangai which we have analyzed fall into the field of an active continental border (Fig. 2). This tectonic category comprises, on the one hand, basins associated with the formation of magmatic arcs, and on the other, "disrupted" basins. Clay-sand trends [24] are used to identify these categories; in the former case, there is a clearcut sand-clay trend running perpendicular to the boundaries of the particular fields, whereas in our case this trend, as reflected in the orientation of the rounded districts of argillites and aleuroites, has an opposite trend and is associated with the dimension of the fragmental material; an increase in the proportion of the quartz aleurite leads to a growth in silica and a reduction in the potassium-sodium ratios. The association of fragmental rocks formed in a "disrupted" basin and the intraplatform volcanites underscore, in an unambiguous way, the rifting nature of a sedimentation basin.

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TECHNOGENIC OXIDATION CHANGES IN REDUCED URANIUM-BEARING SANDY DEPOSITS OF MARINE GENESIS

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UDC 552.51:553.495

The authors studied technogenic redistribution of material under the influence of oxidation processes at a testing ground for oxygen-bicarbonate underground leaching of uranium from ores of an infiltration sheet deposit. They compared the scales of natural and technogenic removal and introduction of material in the system under consideration. A technogenic geochemical reduction barrier restraining extraction of uranium from underground was established, and also an effect of acidification of technogenic solutions, which is connected with oxidation of organic matter and sulfide minerals by technical oxygen.

Natural oxidation transformations of terrigenous gray-colored (reduced) deposits of artesian basins' aquifers in the process of formation of sheet infiltration uranium ore have been discussed repeatedly in the pages of the journal *Lithology and Mineral Resources* [6, 7, 13, 15, 18] and have been described most fully in monographs [3,19]. At the same time, technogenic redistribution and removal of material from ore-bearing horizons as a result of the use of technological schemes for underground leaching (UL) employing technical or atmospheric oxygen has not been studied much, mostly by foreign researchers.

In [23] and other works preceding the publication of [21], primary attention was given to the interaction of carbonate solutions, with variable partial pressure of oxygen, with oxides of U (IV), which were obtained by high-temperature synthesis. In this case, oxidation changes in ores and ore-containing rocks were not studied. The merit of the authors of [21] is that for the first time they used original technical and methodological procedures for taking samples of ore-bearing rocks from well cores, as well as in conducting laboratory experiments on dissolution of uranium, its geochemical companions, and sulfides, while preserving the rocks' original oxidation-reduction condition in all stages of the investigation. In these investigations, ore-bearing, feldspar-quartz, unlithified sands containing calcite (20%) and smectite (15%) were studied. The main reducing agents of oxygen were pyrite, marcasite, ferroselenide, pitchblende, and jordisite. Of iron disulfides, pyrite predominated, amounting to 62-92% of their total. The absence of organic carbon in the ores was specific.

These investigations made it possible to reveal the following features of the process: a) along the filtration path of ammonium-carbonate solutions saturated with technical oxygen under pressure of 689 kPa, from the region of injection to the region of relief, technogenic geochemical zonality is formed in the system: a contracting zone of reduced rocks unaltered by technogenesis, a zone of active consumption of oxygen for oxidation of U and Mo, and a zone of slowly occurring reactions of oxidation and dissolution of Fe sulfides; b) as the rate of dissolution of polyvalent elements with the participation of oxidation-reduction reactions decreases, they form the following series: Mo (IV), U (IV), Se (II), and S (II).

Experimental study of technogenic processes in the laboratory possesses a significant shortcoming in comparison with natural investigations: it is impossible to reproduce the actual biogenic and biochemical situations in it, since a large number of oxidation-reduction processes in the zone of hypergenesis take place with the direct or indirect participation of underground microflora. In the abiogenic low-temperature (<100°C) region, sulfide sulfur is not oxidized at all [14], at least in a time commensurable with the duration of technogenic action on the geological environment. In connection with this, the investigation results given below are based exclusively on natural observations of physicochemical processes occurring underground.

*Deceased.

The object of investigation was one of the ore beds of the Southern Bukinai deposit (Uzbekistan). At the regional level, the deposit is confined to the Kampan aquifer of the Kenimekh artesian basin of the graben-syncline type. Its basic feature is a spatial, genetic, and morphological connection of ribbon (in plan) and roll-shaped (in cross section) ore beds with the region of wedging-out of zones of sheet oxidation (ZSO). Geomorphologically, it is located in a relatively flat space adjacent to the massif of Southern Nuratau; geostructurally, it is localized in slightly dislocated, water-permeable rocks of the platform mantle, which form depression structures in the suborogenic region bordering alpine, postplatform mountain formations.

The territory's Variscian folded basement complex is represented by Silurian, Devonian, and Carboniferous metamorphized terrigenous and carbonate rocks, broken through in places by granite intrusions of Late-Paleozoic age. The ore-bearing horizon under investigation is separated from the basement complex by terrigenous strata (with a total thickness of about 300 m) of deposits of the Cenomanian, Turonian, Coniacian, and Santonian. Higher up in the cross section, above the Kampan horizon, lie Maastrichtian sands changing to limestones, which are replaced by carbonate rocks of the Paleocene, sandy-clay marine deposits of the Eocene, and Oligocene red-bed strata of varying grain size, with a total thickness of ≈ 100 m.

According to a number of ore-controlling traits and the absence of facial control of ore formation, A. K. Lisitsin classified the deposit as the genetic type of epigenetic, sheet, infiltration uranium deposits formed with the participation of gaseous reducing agents. The ore bed is localized in sandy deposits formed in conditions of a marine shoal.

Natural and technogenic geochemical processes were studied in the field according to a unified procedure [8, 12]. From freshly extracted cores, right at the well, using various methods of conservation and sealing, we took rock specimens while preserving their natural structure and oxidation-reduction condition. From these specimens, by the method of evacuation, we extracted the pore solutions. In them, we measured pH and determined the content of K, Na, Ca, Mg, Fe, U, Si, Cl, and SO_4 (analyst L. S. Shulik). In rock specimens taken in a CO_2 atmosphere, we determined acid-soluble (in 6 N HCl) valence forms of U and Fe. In tightly sealed pastes, we measured the pore solution's pH-Eh equilibrium with the rock. After cementation of the sands with epoxy resin, we prepared transparent sections. We determined the gross concentrations of individual components (Ca, Mg, U, CO_2 , S_{sulf} , and SO_4) in the rock.

In studying technogenic geochemical processes, in addition we used the method of hydrogeochemical testing of solutions at the inlet (injection wells) and outlet (relief wells) from the ore-bearing horizon. In observation wells, with the use of polarographic and potentiometric logging, we measured T, pH, Eh, and dissolved O_2 [5]. In samples of the solutions, we measured pH and Eh. We used the following methods of determining the components: volume titration (HCO_3 , total CO_2 , Ca, Mg, Fe, and Al), flame photometry (Na, K, Rb, and Li); photolorimetry (SO_4 , NO_3 , NH_4 , Si, P, Mn, Ti, V, W, and Mo), atomic-absorption spectrometry (Zn, Pb, Co, Cu, Cd, and Ag), laser luminescence and photolorimetry (U), colorimetry with butyl alcohol (Re), emission spectral analysis with excitation of the spectrum in plasma (La, Y, Ce, Nd, and Be), neutron-activation analysis (Cr, Sc, Yb, Eu, Tb, Th, Sb, Cs, Se, and As), and spectral quantitative analysis with excitation of the spectrum in an electric arc (Sr, Ba, and Ga). Organic carbon C_{org} in the rocks was determined by the method of thermal analysis.

Gray-colored, reduced, terrigenous deposits possess two basic integral properties: reduction and neutralization capacities. Each of them cumulatively determines the rocks' neutralization and reduction ability in relation to the most common reagents occurring in natural conditions or used in exploiting ore beds by UL. However, if there is a method for evaluating the neutralization capacity of rocks in relation to sulfuric acid that takes into account all of the rocks' main mineral neutralizers in the form of a kinetic function [9], then the often-used method of permanganate oxidizability for evaluating the reduction capacity of rocks, expressed in mg of O_2 per gram of rock [8,12], does not determine all of the reducing agents capable of being oxidized by oxygen. First of all, MnO_4 and O_2 in equal oxidation-reduction equivalent amounts possess different oxidation ability. Secondly, permanganate, being an antiseptic, oxidizes material without the participation of microorganisms, while oxygen activity rises significantly in their presence. Thirdly, the noncorrespondence of laboratory experiments with permanganate to real oxidation changes in rocks with the participation of oxygen is connected with their brevity, which is not compensated by an increase in temperature by 2-3 times (50°C) [12] in comparison with the actual temperature conditions of groundwaters in ore-bearing horizons. Apparently, these factors explain the selective oxidizing action of permanganate on reducing agents in the rock, which are mostly organic matter, Fe (II) in the composition of aluminosilicates and carbonates, and also in the form of impurities in the minerals. As we can see in Fig. 1, S (II) is practically not oxidized by this reagent.[†]

[†]In the present work, permanganate oxidizability is expressed in % of O_2 by weight.

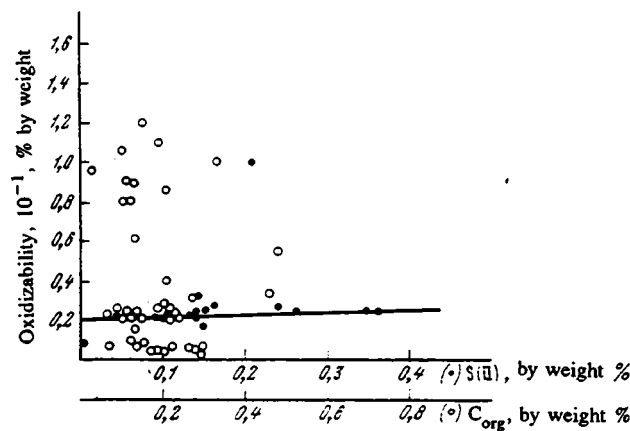


Fig. 1. Effect of contents of sulfide sulfur and organic carbon in sands of the Kampan ore-bearing horizon on amount of permanganate oxidizability.

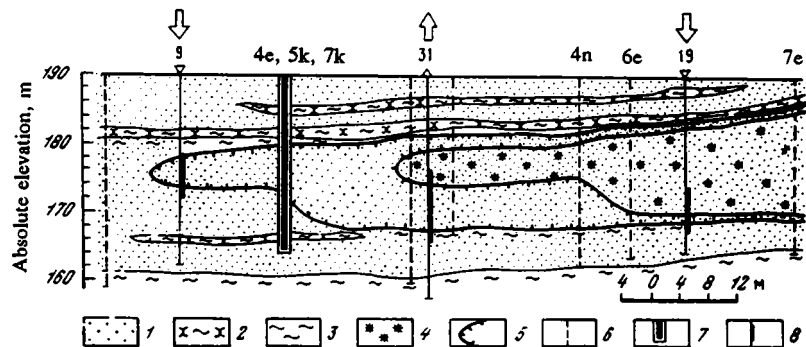


Fig. 2. Cross section of Kampan ore-bearing horizon in the region of the testing ground, within the bounds of which the oxygen-bicarbonate method of underground leaching of uranium was evaluated: 1) greenish-gray, reduced sands; 2) sandstones on clay-carbonate cement; 3) silty clays; 4) greenish-yellow, partially oxidized sands; 5) contour of balance ores; 6) exploratory wells; 7) section in which technogenic oxidation changes in gray-colored sands were studied; 8) development wells (the arrows indicate injection and relief wells).

To determine the forms in which truly dissolved components are found in natural and technogenic aqueous solutions, and to evaluate their degree of saturation in relation to typomorphic minerals, we used the "Karst" program. Presently available software for solving such problems is based on calculation of equilibrium constants, and the algorithms of these programs include exhaustion of all possible reactions in a homogeneous system (the WATEQ and MIF series [11]). For multicomponent systems, such an algorithm is not efficient. Moreover, the system's stoichiometrically fixed composition is a shortcoming of these programs. The "Karst" program uses an algorithm based on minimizing the system's Gibbs function [1]. The thermodynamic constants needed for the calculation are taken from [22, 24].

The scale of natural redistribution of material and changes in typomorphic geochemical parameters was evaluated by comparing various epigenetic geochemical zones; and of technogenic redistribution, by the method of conjugate samples. In the latter case, control wells were drilled with the core close (no more than 5 m) to exploratory ones, which made it possible to compare the original properties with the altered properties of sandy deposits and pore solutions.

The original properties of sandy deposits of the ore-bearing horizon and natural groundwaters unaltered by technogenesis were studied according to the cores of exploratory and development wells. The horizon was bounded by

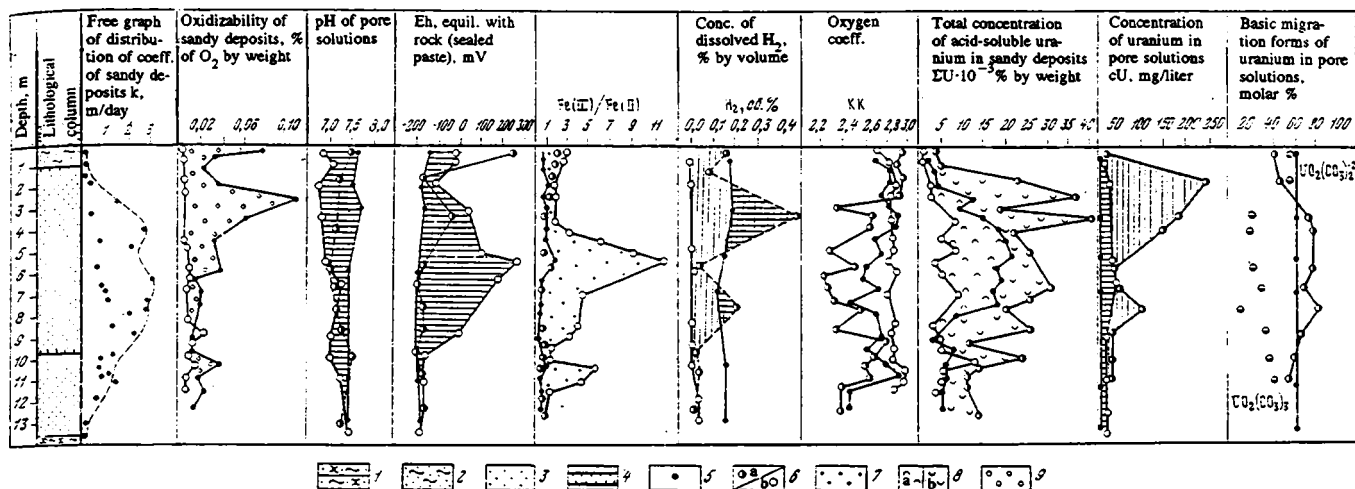


Fig. 3. Technogenic oxidation changes in greenish-gray sands in the process of underground leaching of uranium with the use of technical oxygen: 1) sandstone on clay-carbonate cement; 2) clay, fine-grained, greenish-gray sands; 3) the same, fine- and micrograined; 4) contour of ore body; 5-6) observation points: 5) original, properties unaltered by technogenesis, 6) altered properties of sands at times of 45% (a) and 65% (b) extraction of uranium from the underground; 7) technogenic limonitization; 8) redistribution of uranium (a – removal and b – introduction); 9) change in the sands' permanganate oxidizability.

water-confining rocks: on top, by a layer of sandstones on clay-carbonate cement; and on the bottom, by clay-siltstone formations (Fig. 2). The permeable rocks, with a thickness of 20 m, are divided into two rhythms by a thin layer of lenticulating sandstone, in places changing to clay silts. The upper rhythm, 14-16 m thick, contains ore.

The sands of the horizon's upper rhythm are fine- and micrograined in granular composition, and glauconite-quartz-feldspar in mineral composition. They contain a small amount of mica, primarily muscovite, fragments of siliceous rocks, and titanium-containing minerals (ilmenite, leucogene). Clays in the sands are hydromica-kaolinite.

Toward the roof and foot of the rhythm, the content of aleuropelite in the sands rises, and thin interlayers of clay appear. As a result of such a distribution of sandy-clay material, the rhythm's relatively homogeneous sands have a distinctive seepage structure (Fig. 3), which predetermined the formation of epigenetic geochemical zonality. Processes of sheet oxidation and ore formation took place most intensively in rocks with the maximum permeability, which is characteristic of deposits of the genetic type under consideration [7]. The limbs of the roll are squeezed out by the ore-forming flow of groundwaters into less permeable rocks of the rhythm's roof and foot.

In all epigenetic zones, single crystals of calcite (0.2-0.3 mm) are found in the rhythm's sands, cementing clastic grains. Accumulations of dolomite rhombohedra are found less often; the size of individual crystals is 0.02-0.03 mm. The carbonate content of the sandy deposits is equal to 0.5-3.0%. It rises toward the roof and foot of the rhythm (Fig. 4) and is mostly due to calcite. The dolomite content in the sands does not exceed a few tenths of a percent. Comparison of the amount of carbonate content between zones of oxidized and reduced sands indicates the absence of noticeable redistribution of this material in the natural geochemical zonality (see Figs. 4 and 5).

Segregations of glauconite in the zone of reduced, greenish-gray sands have a rounded or oval shape; sometimes they form small sections cementing clastic material. They are often spatially connected with segregations of pyrite in the form of fine insets inside the grains or on their surface. Larger segregations of pyrite have a rounded shape or are isometric, if they consist of concretions of crystals. Sometimes pyrite globules are situated along microcracks in clastic grains. The contents of sulfide sulfur and total Fe (II) almost do not change through the rhythm's cross section, % by weight: S (II) 0.1-0.2, Fe (II) 0.14-0.22. In the subzone of partial oxidation, in greenish-yellow sands, the content of S (II) drops to 0.01-0.02% by weight; and of Fe (II), to 0.05% by weight. In this case, natural oxidation processes do not destroy organic matter. The content of C_{org} in reduced sands was at the level of 0.05-0.22% by weight, reaching 0.56% by weight under the roof of the rhythm (see Fig. 4), while in oxidized sands it is much lower: 0.06-0.16% by weight (see Fig. 5). This is a specific geochemical peculiarity of the given ore-bearing horizon, which distinguishes it from other horizons containing ore beds of deposits in the Central Kyzylkum [3, 7].

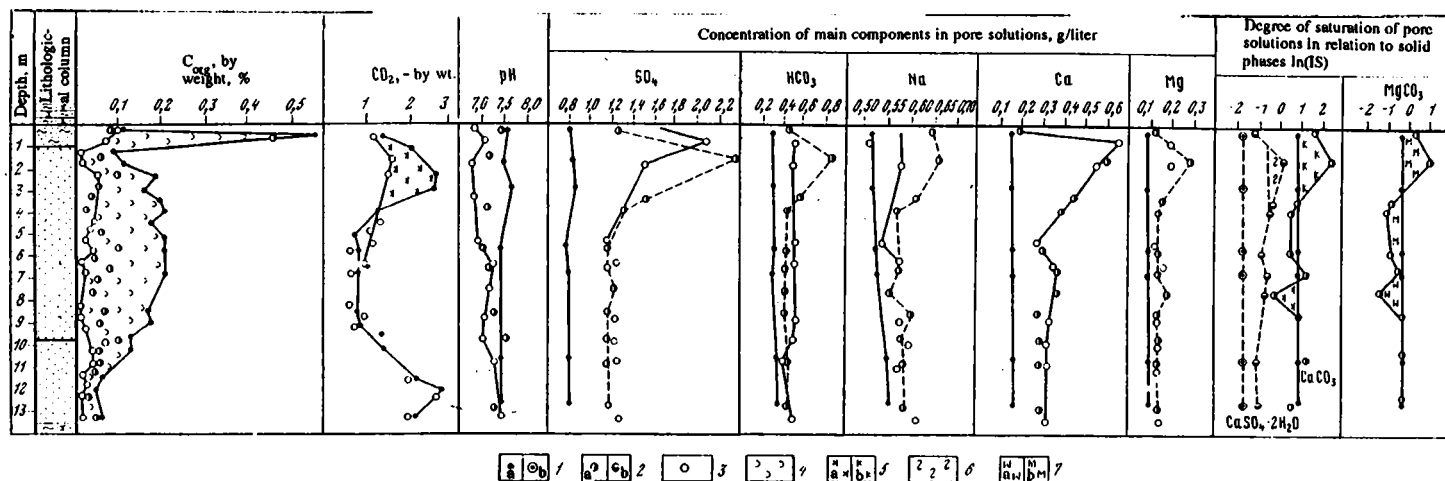


Fig. 4. Changes in contents of organic carbon and carbonate CO₂ in greenish-gray sands of the upper rhythm of the ore-bearing horizon, pH, and concentration of macrocomponents in pore solutions in the process of underground leaching of uranium with the use of technical oxygen. 1-3) observation points: 1) original properties unaltered by technogenesis (a - CaCO₃, b - CaSO₄·2H₂O), 2) altered properties of sandy deposits and pore solutions at the time of 45% extraction of uranium from underground (a - CaCO₃, b - CaSO₃·2H₂O), 3) the same at the time of 65% extraction of uranium; 4) oxidation of organic carbon; 5) redistributions of carbonates (a - removal, b - introduction); 6) technogenic gypsification; 7) redistribution of magnesite (a - removal, b - introduction). See Fig. 3 for the rest of the conventional notations.

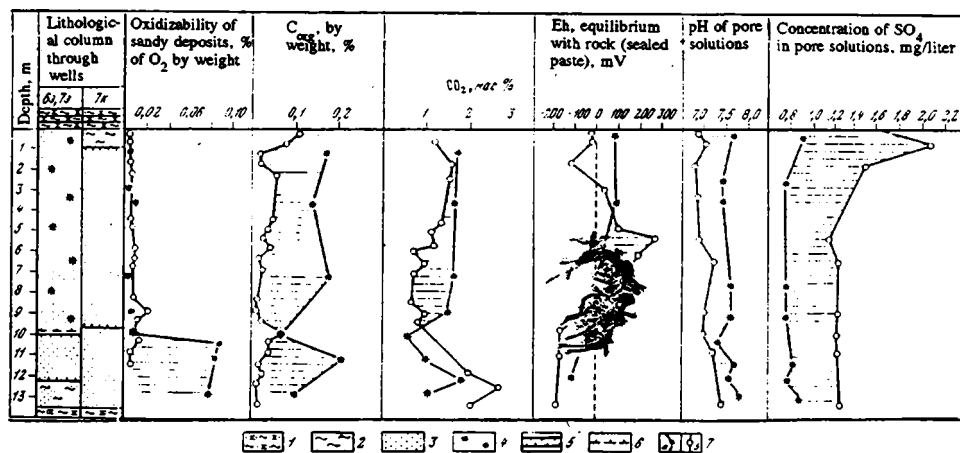


Fig. 5. Comparison of natural and technogenic oxidation changes in reduced sands for wells 6e and 7e from the subzone of natural partial oxidation and for well 7k from the zone of partial technogenic oxidation of greenish-gray sands: 1) sandstone on clay-carbonate cement; 2) clay, fine-grained sand; 3) greenish-gray sand; 4) natural limonitization; 5) contour of ore body; 6) contour of wedging-out of the zone of sheet oxidation; 7) graphs of changes in typomorphic geochemical properties of naturally (a) and technogenically (b) oxidized sands through the depth of the horizon.

In the section where ore-containing greenish-gray sands are developed, the reduction capacity rises from the foot to the roof (from 0.01 to 0.12% of O₂ by weight). As a result of natural oxidation processes, the value of this parameter in the subzone of partial oxidation does not exceed 0.025% of O₂ by weight.

Uranium mineralization is represented by finely dispersed pitchblende, which has all forms of microdistribution in sandy deposits: film, spotty, impregnated, and dispersed. According to data from electron microscopy, in ore bodies leucoxene, leucoxenized ilmenite, and, to a lesser degree, glauconite contain uranium. The bed's ores are lean; hexavalent uranium predominates in them (68% of total U); and the oxygen coefficient of pitchblendes varies from 2.5 to 2.9 (see Fig. 3). The Eh, measured in sealed pastes, decreases with the transition from the subzone of partial oxidation (0 to +90 mV) to the ore zone (-150 to -185 mV). In greenish-gray sands, acid-soluble total Fe amounts to 0.032% by weight, and the portion of its bivalent form averages 54%.

Study of sands from the subzone of partial oxidation in transparent sections showed that occasional clay balls and interlayers remain gray-colored, but there is usually a bright ochreous fringe at the contact with the sand. Fine, light-yellow margins of Fe hydromicas surrounding clastic grains were noted. Near the boundary of wedging-out of the ZSO, pyrite does not have signs of oxidation, but closer to the back boundary of the subzone of partial oxidation it is found less often, and its relicts are surrounded by red-orange Fe hydromicas. In the same direction, brighter-colored ochreous aureoles appear more often around clastic grains, and iron hydromicas cover grains of glauconite in spots or accumulate around them.

In limonitized rocks, the uranium content is 0.0006-0.0015% by weight. According to data from *f*-radiography, tracks are clearly confined to accumulations of iron hydromica.

Sulfate minerals are not found in the horizon's sands. The absence of gypsum in the rock is confirmed by physico-chemical calculations, from which it follows that the pore solutions are incompletely saturated in relation to it. Their saturation index (IS) [20] in the form of the simple ratio of the product of active concentrations of free calcium and sulfate ions to the tabular value of the solubility product of gypsum is equal to 0.17.

As we can see from the data given above, oxidation of Fe disulfides and Fe (II) in aluminosilicates occurs by natural oxidation processes with the participation of oxygen in infiltration waters; however, this does not lead to acidification of groundwaters. Comparison of the pH of pore solutions from the subzone of partial oxidation (see Fig. 5) and from the zone of reduced uranium-bearing sands (see Fig. 4) shows that this index is in a narrow range of values of 7.4-7.6.

The original hydrogeological conditions unaltered by technogenesis are characterized by the following parameters: depth of water table 46 m; formation pressure rises from the roof of the rhythm to its foot from 5.3 to 6.7 atm; seepage of groundwaters in the natural flow occurs at a rate of several meters per year; the temperature of formation waters is

TABLE 1. Chemical Composition of Natural Waters and Technogenic Solutions from the Kampan Ore-Bearing Horizon

Component	Natural water	Productive solutions	
		oxygen-bi-carbonate UL	sulfuric-acid UL
SO ₄	800	1290	9710
Cl	630	710	603
HCO ₃	256	510	0
Total CO ₂	128	250	0
NO ₃	<6	<6	275
SiO ₂	18	12	114
Na	530	670	440
K	14	14	120
NH ₄	0,6	3,2	188
Mg	80	168	1750
Ca	160	340	520
Sr	1,25	1,70	2,79
Fe(II)	<0,05	<0,05	202
Fe(III)	<0,05	<0,05	279
U	0,04	70	15
Mo	4	1650	38
Cr	320	700	140
Mn	<10	450	25400
Ba	130	250	420
Ti	<100	160	360
Li	90	160	190
Pb	150	120	600
Co	70	90	1200
Zn	60	70	2700
Rb	10	50	400
Re	<10	25	350
Cd	19	20	70
Ag	4	6	40
Th	<5	5	<10
PO ₄	<30	<30	4620
La	<50	<50	600
Ni	45	<50	1120
Cu	16	<20	110
Al	<25	<25	900
V	<20	<20	300
Te	<20	<20	540
Os	<10	<10	105
Se	<5	н.д.	146
Sc	<10	<10	188
Y	<10	<10	1040
Cs	<10	<10	16
Be	<1	<1	87
W	<3	<3	<3
As	<1	<1	<10
Sb	<2	<1	<10
Mineralization, g/liter	2,5	4,1	17,0
pH	7,4	6,95	3,45
Eh, мВ	315	345	485

Remark. Contents of SO₄, Cl, HCO₃, total CO₂, NO₃, SiO₂, Na, K, NH₄, Mg, Ca, Sr, Fe (II), Fe (III), and U are given in mg/liter; the rest of the components, in μg/liter.

23°C. In chemical composition, the groundwaters are sulfate-chloride, calcium-sodium (Table 1). They are saturated in relation to calcite and dolomite (IS approximately 1), almost saturated in relation to magnesite (IS = 0.65), and far from equilibrium with brucite (IS = $7 \cdot 10^{-5}$).

Technogenic oxidation changes in sandy deposits of the ore-bearing horizon were studied within the bounds of the testing ground, which is an operational cell of two injection wells and one pumping-out well (see Fig. 2). The cell was part

of an operational unit that consisted of 22 technological wells drilled in rows. The ore bed was exploited for 4.5 years: for the first 2.5 years with solutions of ammonium bicarbonate (1.5-3 g/liter) in a mixture with technical oxygen, and for the last two years with the use of oxygen alone. Control wells were drilled in two stages: 3.2 years (45%) and 4.3 years (60%) from the beginning of extraction of uranium from underground, during the period when oxygen alone was being used for technological UL.

The calculated concentration of O_2 , determined according to the amount of solutions and oxygen fed into the injection wells, was at the level of 70-320 mg/liter. In reality, according to the results of polarographic logging in observation wells near the injection wells, the concentration of dissolved O_2 did not exceed 80 mg/liter. The oxygen entered the ore-bearing horizon through injection wells under pressure, where special dispersers were used to increase its solubility. However, due to relatively slow dissolution of gaseous O_2 in the water, it was not a homogeneous solution that entered the horizon, but a heterophase gas-liquid mixture. This led to a situation in which, as a consequence of its lower density in comparison with groundwaters, it "floated up" toward the roof of the horizon. As a result of this, technogenic oxidation processes took place most intensively under the roof of the horizon, which was primarily reflected in the manifestation of stronger yellow coloring in the originally yellowish-gray sands than on the average in lower parts of the horizon.

The average rate of seepage of technogenic solutions was 0.4 m/day. Against this hydrodynamic background, the dynamics of oxidation of reduced greenish-gray sands in the upper part of the rhythm was characterized by the following parameters (see Figs. 3 and 4): permanganate oxidizability was reduced from the original value of 0.12 to 0.005% of O_2 by weight; oxidation of organic carbon from 0.22-0.56 to 0.001-0.005% by weight occurred; the Eh, measured in sealed pastes, rose to +300 mV, the amount of which agrees well with data from potentiometric logging; and the content of acid-soluble Fe (III) increased — the value of Fe (III)/Fe (II) reached 12. Oxidation of sulfides and organic matter is connected with the appearance of sulfuric and carbonic acids, which was accompanied by a reduction in pH from 7.4-7.6 (in natural waters) to 6.7-7.2 (in technogenic solutions) and by a rise in the concentrations of sulfate and hydrocarbonate to 2.4 and 0.9 g/liter, respectively. An increase in the solutions' aggressivity in relation to the sandy deposits led to leaching of Na from them and to dissolution of carbonate minerals, which was accompanied by a rise in the concentration of Ca and Mg (see Fig. 4). Computations by the "Karst" program showed that in the region of maximum generation of technogenic solvents transfer of a number of components occurred in a saturated or supersaturated state. Along with the actually established destruction of carbonates under the action of sulfuric-acid solutions occurring as a result of oxidation of sulfides, in these sections of the horizon formation of technogenic gypsum is theoretically possible, and dissolution of carbonates is possible, followed by redeposition at a neutralization geochemical barrier when the solutions move into the region of rocks not technogenically oxidized. This is indicated by graphs of the distribution of the solutions' $\ln(IS)$ with products of dissociation of calcite, magnesite, and gypsum through the depth of the horizon (see Fig. 4).

In the system under consideration, mass transfer of uranium in the region where reduced, gray-colored deposits are found occurred with redeposition at a mobile reduction geochemical barrier. The parameters of this barrier were studied in a section located 14 m from an injection well, 3.2 years from the beginning of the process (see Fig. 3). In this section, simultaneous removal and accumulation of uranium are noted: removal under the roof of the horizon (the maximum concentration of U reached 250 mg/liter), and introduction in the base part of it. Judging from the results of analysis of dissolved gases (O_2 , CO_2 , CH_4 , H_2), hydrogen was the reducing agent for uranium. Its content was $\approx 2-4$ times higher (0.45% by volume) in comparison with the natural background (0.1-0.2% by volume). The occurrence of gaseous hydrogen is apparently of a mixed biochemical and purely chemical nature. Occluded hydrogen in carbonate minerals could be released when they dissolve, and it could also occur as a result of hydrogen microbiological fermentation [3]. The oxidation-reduction potential in this section of the horizon does not differ significantly from the natural values, rising in the direction toward its roof from -150 to -200 up to -50 mV, and to +250 mV directly under the roof. Transfer of uranium in the conditions under consideration, in spite of the predominance of sulfate ions over carbonate ones, occurred in the form of uranium tri- and dicarbonate complexes; in this case, the latter predominated in slightly acidic solutions, and the former in close to neutral ones.

In the region of maximum concentration of uranium at a technogenic reduction geochemical barrier, the content of it reached 0.042% by weight. The oxygen coefficient of uranium oxides had values of 2.2-2.3, which is significantly lower than its value in natural oxides and directly indicates the depth of reduction processes occurring in technogenic conditions. The existence of such a barrier in the geotechnological process indicates the presence of a powerful restraining factor in extraction of uranium from underground. This is one of the reasons for the slower occurrence of the process of UL of

uranium with the use of bicarbonate-oxygen and oxygen technological schemes in comparison with the sulfuric-acid one in analogous conditions, but in ores with $\text{CO}_2 < 1\%$.

Field description of the sandy rocks and study of them under a microscope showed that technogenic oxidation processes lead to a change in reducing rocks analogous to their natural predominance in the subzone of partial oxidation described above.

On the whole, on the basis of the lithological and geochemical investigations that were conducted, we can conclude that the technogenic oxidation process is largely similar to the natural one. As in natural conditions, at the end of the zone of technogenic oxidation of rocks a zone of uranium accumulation forms. The only difference consists in the rate of oxidation of individual reducing materials and in the depth of oxidation transformations (see Fig. 5). No differences at all are recorded in the amount of permanganate oxidizability. In this case, the Eh of equilibrium with the rocks in local sections exceeded the natural background by 200 mV, while on the whole being in the region of lower values in comparison with it. The most contrasting are technogenic changes in the content of C_{org} in the rocks, pH, and the concentration of sulfate sulfur in the pore solutions.

As was noted above, in the process of natural oxidation of the rocks acidification of formation waters is not observed (see Figs. 3 and 5). This is fundamentally significant, since the phenomenon of redistribution of monovalent chemical elements in the region of transition from partially oxidized rocks to reduced ones has been vigorously discussed recently. Publications with directly opposite content have appeared. Some of them indicate a significant role of an acid-alkaline barrier in accumulation of rare-earth and other groups of elements, which is spatially connected with the mobile oxidation-reduction boundary [16-18]; others doubt the geochemical significance of such a barrier [9, 10]. In the studied lithochemical conditions of an ore-bearing horizon composed of marine, glauconite-quartz-feldspar sands with relatively low sulfide content, in the case of technogenic oxidation, with which an effect of acidification of groundwaters by 0.8 pH unit was established instrumentally in natural conditions, the following chemical elements become mobile (the increment in concentrations over the natural background was computed according to the data given in Table 1), $\mu\text{g/liter}$: Re 25, Rb 40, Ti 60, Li 70, Ba 120, Cr 380, Mn 440, Sr 450, and Mo 1645, and technogenic redistribution of them is possible in these acid-alkaline conditions. Comparison of the chemical composition of natural waters and technogenic solutions (see Table 1) shows that, within the limits of sensitivity of methods of chemical analysis, removal of Cs, Ni, Cu, Pb, Cd, W, Ag, V, Ga, Be, Al, Sc, La, Ce, Y, P, As, and Sb from the horizon's rocks was not noted. Many of these elements pass into the liquid phase only in sulfuric acid solutions with pH 3.45. The latter data were obtained from results of testing of productive solutions within the bounds of the unit of sulfuric acid UL carried out in the same ore-bearing horizon.

Comparative analysis of natural and technogenic oxidation changes in reduced sandy deposits makes it possible to note the following. In contrast to natural oxidation processes, which are characterized by slow dynamics due to the relatively low seepage rates (a few meters, sometimes a few tens of meters per year) and gradients of the oxidizing agent's concentration ($\text{CO}_2 < 8 \text{ mg/liter}$ [3]) determining a rate of progress of the oxidation-reduction boundary of fractions of a meter or a few meters in 1000 years [4] and a long duration of formation of subzones of partial sheet oxidation (from tens of thousands to a few million years [2, 3]), technogenic oxidation geochemical zonality is formed in significantly shorter time intervals, as a consequence of higher hydraulic and concentration gradients. With a seepage rate of 150 m/yr and a concentration of O_2 of about 80 mg/liter, the rate of progress of the boundary of wedging-out of the zone of technogenic oxidation is estimated as 4 m/yr, which is approximately four orders higher than the rate of progress of the natural oxidation-reduction boundary at deposits of the genetic type under consideration.

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LITHOLOGY AND FACIES OF QUATERNARY DEPOSITS OF THE RUSSIAN COAST OF THE CASPIAN

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UDC 552.51:551.7.022:551.79

In the article, we discuss the spatial distribution, structure, and composition of Quaternary sediments of the Russian coast of the Caspian. The exceptional diversity of facial composition and wide distribution of sediments of mixed and complex origin are emphasized. The presence of specific facies devoid of clear analogs ("chocolate clays," the knoll sequence, and recent sediments formed in extensive shoals with hydrophyte vegetation) is noted. It is shown that different facies form different facies sequences along the section and over the area, reflecting changes in the sedimentation regime laterally and over time.

The uninterrupted rise of water level in the Caspian Sea over the last decade caused substantial changes in the appearance of the coast. The shoreline moved deeper into the territory, reaching 10 km or more into the lowland areas of Kalmyk. This was accompanied by changes in the coastline configuration, the dynamics of coastal processes, and coastal landscapes. The degree of transformation of the shore face in many ways depends upon the composition of the rock composing it. The Caspian coast within the Russian Federation is almost exclusively composed of unconsolidated Quaternary deposits of diverse origin and lithological composition (clays, silts, siltstones, loams, loamy sands, sands, and pebbles). The deposits are characterized by different degrees of diagenetic transformation (from semiliquid, dispersed regolith in the Volga Delta and at the bottom of the Caspian to densely lithified Upper Khazar detrital limestones and conglomerates), but weakly altered unconsolidated varieties of rock predominate over all.

The lithological features and facies of the Quaternary deposits of the Caspian coast have been insufficiently and unevenly studied. Aside from on-going research on the Volga delta [5], bottom deposits of the Northern Caspian [10], and individual thematic investigations [1, 8, 9], extensive areas of the Kalmyk coast remain almost unstudied from a lithological point of view and need further investigations.

From a chronological point of view, almost all subdivisions of the Quaternary system (Lower, Middle, and Upper Pleistocene as well as Holocene) can be distinguished among the latest deposits of the coast. In terms of origin, marine formations predominate among the sediments; aqueous deposits formed on land (alluvial, lacustrine, and lagoonal deposits) also compose a substantial portion. Sediments of eolian origin are abundant among especially terrigenous deposits; deluvial and proluvial formations occur locally. The location of the territory in a zone of constant shifting of the land-sea boundary and the presence of the mouths of large rivers (Volga, Terek, Sulak, etc.) on the coast preordained the widespread occurrence of sediments of mixed and complex origin: alluvial-marine (deltaic); lacustrine-marine (liman-lagoon, kultuk), lacustrine-alluvial (lakes in the Volga delta), composed of a multitude of facies succeeding one another laterally and along the section.

The diversity of facial composition characteristic of recent sediments can be traced in the fossil state far less clearly and usually within broader genetic categories.

Among marine deposits, one can distinguish sediments of the Bakin, Khazar, Khvalynsk, and New-Caspian transgressions as well as recent sea floors of the Caspian.

The Bakin deposits are near the Volga Delta. They have been penetrated by holes and are represented by various facies of shallow-water littoral zones (grey, greenish-grey, dense, laminated clays, occasionally with interlayers of fine-grained sands up to 10 m thick or more). Toward the Upward along the Volga valley, the Bakin sediments are sediments of step-to shore Volga estuary; they are exposed at the bottoms of fossil sections of Chernyy Yar and Baskunchak and consist of dense siltstones and occasionally silty dark-grey clays with interlayers of fine-grained sandstones. Mineralogical spectra of the terrigenous component of the Bakin sediments are characterized by a predominance of quartz (up to 60-70%)

in the light fraction. Feldspars constitute up to 10-18% and rock fragments also present. Minerals of the epidote and ilmenite groups predominate in the heavy fraction, reaching 30%. There is a high (up to 18%) content of garnet. Tourmaline, staurolite, sphene, hornblende, disthene, are consistently present; rutile, apatite, zircon, leucoxene, and glauconite are found in smaller quantities. In some especially finely dispersed interlayers, neogenic minerals play an important role. According to the data of Rengarten [8], authigenic iron sulfides can compose up to 95% of the heavy fraction and clay aggregates can constitute up to 80% of the light fraction. The clay material of these consists of a mixed-layer component of montmorillonite-hydromica, hydromica, kaolinite, and chlorite-vermiculite.

In submontane Dagestan, the Bakin sediments are represented by dynamic shallow-water formations. They compose a high marine terrace and consist of detrital sands, conglomerates, and, occasionally, sandy clays. They contain abundant fauna of brackish-water *Didacna*, form a high (up to 200 m) marine terrace. They are 8-10 m thick. In the Terek-Sulak lowland, the thickness of sediments increases to 150 m; these sediments are composed of light-gray calcareous sandstones grading into sandy clays.

The Khazar marine deposits within the Volga delta and Kalmyk are also known only on the basis of drilling data and suggest a calm depositional environment. In composition, these are clays and loams; they are dense and contain interlayers of fine-grained sands characterized by fossil assemblages of marine molluscs. In fine facies of Khazar sediments containing the 1.0-0.1-mm fraction, this fraction constitutes 0.2-3.5%; the 0.10-0.05-mm fraction constitutes 7.6-69.8%; the 0.05-0.01-mm fraction constitutes 2.9-52.0%; and the fraction smaller than 0.01 mm constitutes 7.4-58.8% [5]. In the bottom part of the section, gray tones predominate, locally with bluish or reddish-brown tints. Sandy loams with barnacle shells tinted blue (vivianite?) are sometimes found in the lower part of the section. In the upper horizons the abundance of shelly material decreases, brownish-gray tones predominate, and inclusions of gypsum crystals occur. At the very top, there are numerous rust spots and bands giving the rock a variegated appearance.

Higher-energy conditions of formation, characteristic of shallow water marine environments near river mouths, are typical of the Khazar sediments exposed in sections along the Lower Volga. At the base, they are usually sandy; the middle portion is represented by a packet of gray siltstones with interlayers of sand. Upward along the section, grayish-yellow, fine-grained sands with occasional interlayers and lenses of clay again predominate. In mineral composition, they are similar to the Bakin sediments, being essentially quartz (up to 75%) with a predominance of epidote, ilmenite, and garnet and an admixture of hornblende, zircon, disthene, tourmaline, and staurolite in the heavy fraction; limonite, barite, and pyrite are among the authigenic minerals.

In submontane Dagestan, typical facies of the Khazar deposit indicate a high-energy depositional environment; these deposits are conglomerates with carbonate cement and interlayers of detrital limestone and sandy clays of variegated color. In the Terek-Sulak lowland, the sediments are characterized by a sandy-clayey composition and appreciable thicknesses, reaching 150 m or more.

In general, the deposits of the Khazar Sea are relatively thin, although they contain more sandy material than the Bakin deposits contain.

Lower Khvalynsk marine formations are exceptionally widespread in the Caspian region. In the Volga delta and in Kalmyk, they are usually overlain by a mantle of younger formations; however, they outcrop at the surface in a number of cases (in "Black Earth" regions; in deflation basins, in the Volga delta at the bottoms of Baer knolls undercut by erosion). Somewhat further to the north, within areas of positive surface elevation, they form a marine terrace along both banks of the Volga; they are represented by a stratum of interfingering sand and clays up to 20 m or more in thickness. Yellow-brown fine-grained sands, occasionally with a basal horizon consisting of clay balls lie at the base of the Khvalynsk sediments. In terms of mineral composition, the sands are essentially quartzic (up to 87% quartz; up to 20% feldspar). In the heavy fraction, the magnetite-ilmenite group constitutes up to 35%; epidote, up to 45%; hornblende, up to 30%; garnet, up to 11%; zircon, up to 8%; disthene, up to 5%. Glauconite, tourmaline, and apatite have also been noted [1].

"Chocolate" clays are a typical facies of the Lower Khvalynsk deposits. They are especially characteristic of the Caspian region. They compose a substantial portion of the section of early Khvalynsk sediments and exhibit clear confinement to a time interval, thereby serving as a fine stratigraphic marker. They are also quite localized in space, lying in lows on the bottom of an ancient Volga estuary at absolute elevations ranging from +35 to -20 m. Since the origin of the clays is controversial, we will discuss their lithological characteristics in detail.

The clays are light- or dark-brown (chocolate) in color, with rosy or grayish tints. In terms of mechanical composition, these are the most highly dispersed and finely washed of all sediments found in the Caspian region: particles less than 0.05-0.1 mm constitute 20-35% of the total; particles in the 0.1-0.5-mm range account for 5-25% [5]. Highly dispersed

minerals include kaolinite, montmorillonite, illite, and hydromica. Clayey material is impregnated with hydrous ferric oxides, totalling 2.95-6.14%. Carbonates, chlorides, and sulfates are included in the composition of readily soluble salts. The abundance of carbonates in the clay fractions reaches 7.58%. Chlorides are disseminated in the rock and do not form substantial aggregations. Gypsum frequently occurs in the form of small crystals and druses. The layered texture of the clay is emphasized by different tones of color and the presence of thin interlayers of light-yellow siltstone and sand frequently containing marine molluscan fauna. The composition of molluscs is diverse and characteristic of different stages in the evolution of the Early Khvalynsk transgression. This fact, together with the different hypsometric position of the "chocolate" clays, is not in accord with the idea that the clays were formed in an isolated Khvalynsk Sea [2, 3]. Accumulation of clays took place during various intervals of the early Khvalynsk transgression. Necessary conditions for the formation of such clays included an abundance supply of fine iron-rich particles from the land, particles which settled below the mud line in the step-to shore parts of the marine basin located within an ancient Volga estuary. The layered structure of the clays probably has a different origin (banded lamination of a seasonal type; enrichment with sand particles during penetrations of river currents into the marine basin, etc.).

The Lower Khvalynsk marine sands with gravels and pebbles and occasionally brownish-gray sandy loams and loams, reflecting conditions of a dynamic sublittoral zone, form an accumulative mantle of terraces with absolute elevations of 50-60 m within Dagestan. In the vicinity of Derbent, there is a predominance of clayey sands with pebbles and shells; at the base, there are markedly carbonate-rich sands lying on an abraded surface of Khvalynsk and pre-Quaternary formations. In the vicinity of the town of Makhachkal, clays of variegated coloration and inequigranular sands as well as calcareous sandstones and conglomerates occur among Khvalynsk deposits. In the Terek-Sulak lowland, there is a predominance of clay with interlayers of gray fine-grained sands and, occasionally pebbles. The total thickness of the deposits exceeds 150 m.

The Upper Khvalynsk marine deposits (in contrast to the Lower Khvalynsk) are of more sandy, shallow-water origin. Among the sands occurring on both sides of the Volga delta and in Kalmyk, there is a predominance of very fine-grained and fine-grained silty varieties with the following composition of fractions: 0.5-0.25 mm, 1.3%; 0.25-0.1 mm, 78.98%; 0.1-0.05 mm, 17.68%; 0.05-0.01, 1.1% [8]. Whereas "chocolate" clays are facies specific to the Lower Khvalynsk formations, the types of deposits composing the upper portions of knolls of the *Baer-Sequence* are specific to the Lower Khvalynsk. These deposits are abundant in the area of "dissected deltas" and coincide in time with one of the final stages of the Late Khvalynsk transgression. The majority of Baer knolls (their socles are usually composed of Lower Khvalynsk clays) consist of clayey sands, sandy loams, light loams (yellowish-brown with reddish, yellowish, and rosy tints) up to 22 m in thickness. At the base of the sequence, there are obliquely laminated fine-grained sands. These sands are thin (0.2-2.0 m), with a high percentage (up to 90%) of the 0.10-0.15-mm fraction. Most of the sequence consists of a packet of sands and sandy loams with diverse types of bedding (horizontal, cross, diagonal, and lenticular). Sand-sized particles are often clay balls or broken sheets of "chocolate" clay (dense water-resistant aggregates). The 0.10-0.05-mm fraction predominates (>50%) in the mechanical composition of the sequence; the 0.05-0.01-mm and the fraction less than 0.01 mm are present in roughly equal amounts ($\approx 20\%$). Readily dissolved salt are abundant. Chlorides impregnate the rock but form almost no local accumulations. Sulfates in the form of gypsum compose nests and veinlets. Carbonates are present in the form of concretions and patches as well as finely dispersed admixtures giving the rock a whitish tint. The deposits are unevenly compacted, with high textural density associated with high carbonate content of sediments. In the upper horizon of the sequence, sandy loams predominate; occasionally, there are clayey or silty sands with high content of the 0.10-0.05-mm fraction.

The features of composition, structure, and position of the sequence do not allow us to explain its deposition by the action of any single factor (eolian, marine, or alluvial), though some investigators have tried [3, 4]. Most probably, this formation is complex in terms of origin, and eolian and erosional processes as well as marine processes participated in its creation. Initially, accumulation of the sequence took place within extensive shoals of a regressing Late Khvalynsk sea, where eolian-marine sediments accumulated on highs, conferring an unevenness to the seafloor in the form of hills. Tidal phenomena with currents oriented in the direction of the prevailing winds were active as the sea level dropped but strong winds remained; in addition, an erosional factor emerged. The upper part of the sequence, with steeply inclined layers, formed under these conditions. It is possible that one of the conditions of formation of the Baer knolls and sediments composing them was a specific combination of angles of convergence between numerous branches of the ancient Volga delta and surges of the sea controlled by the position of the ancient shoreline of the Caspian. It should be noted that the depositional environments existing at the end of the Late Khvalynsk transgressions were never repeated.

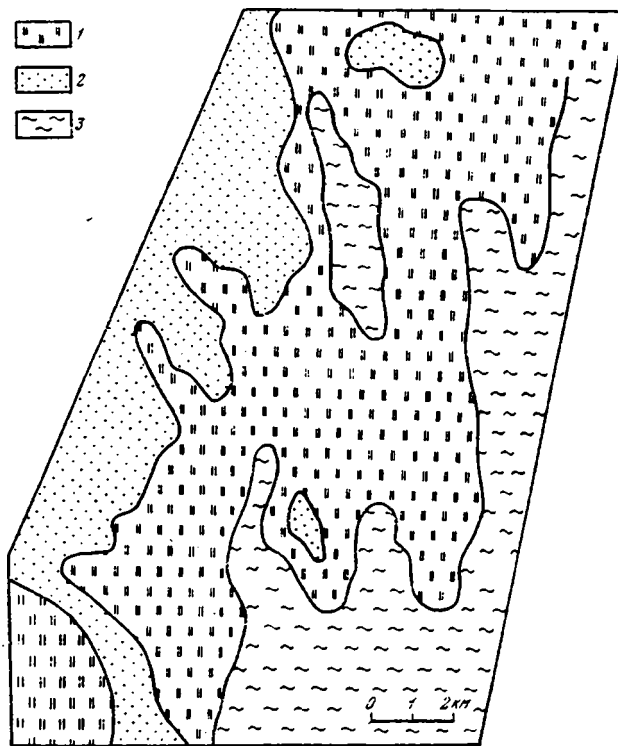


Fig. 1. Distribution of shallow water facies with abundant hydrophyte vegetation on the lowland coast of Kalmyk (in the vicinity of Lagani): 1) area of hydrophyte vegetation; 2) land; 3) sea.

The Upper Khvalynsk marine sediments in Dagestan compose near-shore terraces at absolute elevations ranging from 0 to -20 m. These sediments consist of exclusively shallow water facies: sands with pebbles and gravel, more rarely, sandy loams and loams. To the north, in the vicinity of Kizlyar Bay, Late Khvalynsk sediments consist of dark-gray and brown loams which accumulated in a freshened bay, the mouth of which opened to the northeast. Terrigenous material was supplied by the Terek and Kuma rivers.

Khvalynsk deposits have been found on the floor of the Caspian Sea. In the northern part of the sea, they are fine grayish-brown clayey slightly carbonate silts.

New-Caspian marine sediments predominantly occur along the northwestern coast of the Caspian, up to the Volga delta, where they continue in a belt up to 40 km wide, deeply penetrating to the west and northwest along inter-knoll depressions. They consist of gray fine-grained shallow water sands with various amounts of clayey material, occasionally with interlayers of sandy loams and loams, and with brown patches of iron oxides.

In the Terek-Sulak lowland, the thickness of New-Caspian sandy muds with lenses of coquina reaches 50 m.

On the Dagestan coast from Sulak to Samur, New-Caspian inequigranular shelly sands with pebbles and gravel form the lowest marine terraces and belong to high-energy facies of shoals and beaches. Gray and greenish-gray sands with shells compose step-to shore parts of the Dagestan shelf.

Sands, siltstones, argillaceous muds, and coquinas predominate within the compositions of recent marine sediments of the Northern Caspian. The main source of material is drift of the Volga River, which amounts to ≈ 12.5 million tons per year; the traction load approaches 5-10% of the sediment discharge, with the remainder belonging to suspended material [7].

Within the fore-delta areas of the Volga, fine sands and silty sands are widely occurring. In fine sands, the 0.10-0.05-mm fraction equals 27-40%; the 1.0-0.01-mm fraction equals 55-70%. In silty sands, the 0.10-0.05-mm fraction predominates (55-70%).

Predominantly sandy sediments make up the central part of the aquatory of the Northern Caspian [10]. Extensive fields of coarse siltstone occur in Kizlyar Bay. The terrigenous material in this bay is supplied by drift from the Kuma and Terek rivers. In the near-mouth areas of the Volga and Terek, fine-silt muds are abundant; patches of argillaceous muds

saturated with shell material occur among the fine-silt muds. Extensive shallow water banks are formed by coquinas consisting of shells of both Caspian aboriginal species (*Didacna*, *Monodidacna*, *Dreissena*) and immigrants (cerastoderms, mussels, etc.). Here, the composition of the coquinas is to a great extent determined by the biological productivity of the bottom fauna, primarily, bivalve molluscs.

In general, despite the fairly diverse lithological composition of recent and Old-Caspian marine sediments, there is a definite trend toward a change in their composition along the section, showing the change in depositional environment. Silty-clayey and muddy facies, reflecting calm conditions of formation, predominate among the Bakin deposits; sandy-silty-clayey facies of more diverse origin predominate among the Khazar deposits. Clayey facies filled with water of the Volga estuary are typical of Lower Khvalynsk deposits and sandy, shallow water facies are typical of the Upper Khvalynsk and New-Caspian deposits.

Specific sediment facies associated with abundant development of hydrophyte vegetation and the action of prolonged surges are characteristic of the open low-lying shores, a broad belt extending along the Northern and Northwestern Caspian.

Shallow water facies with hydrophyte vegetation is confined to the nearshore zone of the sea, which is inhabited by thick growths of reeds (*Phragmites communis*), cat-tail (*Typha angustifolia*), occasionally flowering reed (*Butomus umbellatus*), burweed (*Sparganium remosum*), floating heart (*Nymphaea candida*) (Fig. 1). In the absence of an active environment, with stagnant conditions and an abundance of dead plant organics, but with a limited supply of exceptionally fine suspended matter, essentially organogenous formations are formed. These consist of plant remains decomposed to various degrees, with a small admixture of sandy-silty terrigenous material dark gray or bluish gray-gray in color.

Sediment facies associated with prolonged surge action are just as characteristic of and specific to the low lying coast of the northern and northwestern Caspian. Thin layers of silt and mud, precipitated from suspension, and sand particles, dragged along the bottom, accumulate during times of prolonged surges and drops in sea level. The composition of the components is usually similar to that of the underlying rocks and it is almost impossible to distinguish between the two in sections.

Avandelta facies are confined to the frontal part of the Volga delta as accumulation of sediments shifts seaward. The main factors affecting the formation of sediments are river flows, the specific delta dynamics resulting from the natural terrain, and the shallow depths facilitating rapid gas exchange. Silty, occasionally argillaceous sand (more rarely, coarse silt) predominate among the sediments; the presence of vivianite disseminations, shells of brackish-water and fresh-water molluscs, and, more rarely, plant remains are typical. Sands are restricted to areas with the highest levels of flow; they are well sorted (occasionally the content of the 1.0-0.1-mm fraction reaches 90%). One can also find varieties with elevated (up to 83-95%) contents of the 0.10-0.05-mm fraction or with approximately equal contents of the 0.10-0.05-mm and 1.0-0.1-mm fractions [5]. In argillaceous sand, the content of the fraction less than 0.01 mm is elevated (up to 7%). Thin lamination, associated with the seasonal nature of accumulation processes (flood-low water), is characteristic.

Facies formed in limans and lagoons occur along the present-day coast and, in places, along ancient coastlines. They can be differentiated from the beach, spit, and barrier sediments adjacent to them by their finer sandy-silty composition and the presence of a mixed fresh water-brackish water assemblage of molluscs. In the fossil state, these facies are important diagnostic indicators of the positions of ancient Caspian shorelines.

Sediments of lacustrine and flood facies confined to numerous lows to the deep areas the low-lying Caspian coast are similar in lithological composition. They have more carbonate, but do not contain ancient Caspian molluscs. Occasionally, they have been slightly reworked by soil processes.

Playa and solonchak facies associated with closed basins are encountered more rarely. These are thin two-layer sediments, with the top layer consisting of brine salts and the lower level consisting of semi-liquid dark bluish-gray salinized sandy ooze. Chemogenic sediments include common salt (NaCl), epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), astrakanite ($\text{MgSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$), and mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$).

In the Volga delta and western and eastern sub-steppe ilmans, a specific facies of ilman-kultuk sediments is widely occurring. Their accumulation takes place under conditions of semiclosed bays lying between areas of land open to the sea (kultuks) or closed water bodies pinched off from the sea (ilmans). Typically, these are between-knoll spaces where material arrives from the slopes of knolls and, periodically, from seas or branches of rivers. In general, this is a shallow water facies with limited supply of terrigenous material and calm sedimentation. In terms of composition, these are clays, silts, sandy loams which are sandy to various degrees; they are dark gray with bluish-gray or greenish tints, lumpy texture, large quantities of rotted plant remains, shells of fresh-water molluscs, and disseminations of carbonates, chlorides, and

sulfates. The mechanical composition is characterized by insignificantly small amounts of the 0.1-mm fraction; fractions with grains sizes within the ranges of 0.10-0.05, 0.05-0.01, and less than 0.01 mm are present in approximately equal amounts. The fraction greater than 1.0 mm is generally lacking [5]. In sediments of shallow water ilmans, the fraction less than 0.01 mm is sometimes greater than 50%.

Deltaic and alluvial deposits, together with marine deposits, are fairly widely distributed over the Caspian coast. Deltaic deposits of the Volga are primarily represented by fine sands. Channel facies and facies of weakly flowing and periodically flowing water bodies gradually alternating with one another can be found among them. In the mineral composition of the deltaic deposits, quartz predominates in the light fraction (up to 60-70%); feldspar equals 13-23%. Minerals of the epidote group (averaging 26%, varying over a range of 10-49%) and black ore minerals (averaging 26%, varying over a range of 10-48%) play leading roles in the composition of the heavy fraction. Hornblende (averaging 14%), garnet (averaging 7%), as well as zircon and muscovite are present in substantial quantities. One can also find anatase, staurolite, sphene, tourmaline, tremolite, diopside, iron oxides, and biotite. Authigenic minerals include glauconite, celestite; the content of these minerals typically reaches 2%.

Deltaic sediments of the Terek and Sulak rivers are more differentiated in composition, ranging from silty sandy laminated clays with inclusions of plant remains deposited in abandoned branches of rivers, and oxbow lakes to sands and gavel-pebble accumulations forming spits and banks. They differ substantially in mineral composition from Volga sediments. The drift of the Terek River is characterized by elevated contents of pyroxenes (10-30%), hornblendes (10-30%), chlorite (10-30%), and small quantities of persistent minerals (ilmenite, garnet, tourmaline, and staurolite). The drift of the Sulak River is characterized by high contents of iron oxides (up to 60-70%), fragments of mica schists (10-30%), and chlorite (10-30%); there are also individual grains of hypersthene, hornblende, biotite, and epidote [6].

Essentially alluvial formations consist of a combination of facies: fine floodplain sediments, silty sands of oxbows and of backwaters and sands forming channel banks, channel beds, and sandbars. Alluvium of the Volga is distinguished by relatively fine mechanical composition; these sediments are predominantly fine and very fine sands, sandy loams, loams, and, more rarely, clays. Fluvial facies in the lower reaches of the river are usually comprised of well sorted silty sands with a content of the coarse silt fraction reaching 96%. These sediments are gray and eluted, with sparse plant remains. Floodplain (flood-bed) sediments composing substantial bay areas are distinguished by a characteristic layering: thin layers of gray sandy micaceous silty clay with rough spots and brownish-gray micaceous sand, typically with black sooty inclusions of plant remains.

In the Terek-Sulak lowland, the various facies of alluvium are more contrasting in composition, ranging from silty clays and sandy loams to inequigranular sands with pebbles and boulders. Coarse pebbles and conglomerates with calcareous-sandy cement are widely occurring in the alluvium of submontane Dagestan.

Eolian sand facies are fairly widespread within the Late Khvalynsk plain, ancient deltas, and in open beach areas. On the Agrakhan Peninsula in particular, eolian deposits extend in a belt 7-km wide and form dunes up to 5 m high. Diverse land forms (mountain masses, knolls, ridges, and eolian deposits) are characterized by fairly homogeneous mechanical composition: fine sands, more rarely, fine- and intermediate-grained yellowish-brown, diagonally bedded and cross-bedded, with detritus of mollusc shells. Ridge sands fixed by plant cover are typically silty and slightly subject to the desert soil formation.

Slope and proluvial deposits have a fairly restricted distribution on the Caspian coast. Proluvial facies within the Dagestan segment of the coast are characterized by a coarse gravelly-pebbly composition. Deluvial facies are typically poorly sorted, sandy loamy-loamy or sandy with inclusions of parent-rock fragments.

Various facies of the latest deposits of the coast and seafloor form specific facial sequences along the section and over the area; these sequences reflect changes in the depositional regime laterally and over time (Table 1). Sequences can be normal or mixed based on the character of the facies set and the conditions of their articulation. The first consists of facies alternating with one another in natural sequence, without substantial gaps in sedimentation; the second consists of deposits differing markedly in depositional environment and separated by horizons of erosion and breaks in sedimentation.

Normal facies sequences can be "long" or "short." "Long" facies sequences include facies reflecting a sedimentation regime extending for a large distance in a lateral direction. For the most part, the following combinations of facies should be classified under this type: marine shallow water-avandelta-alluvium; marine shallow water-hydrophyte vegetation-lagoon-beach. The following facies are "short" sequences: alluvial-kultuk (ilman); marine-kultuk (ilman); lacustrine-playa; eluvial-deluvial.

TABLE 1. Facies and Facies Sequences of the Latest Deposits on the Russian of the Caspian

Facies and facies sequences			Region		
			Dages- tan	Kalmy- kiya	Volga del- ta
Normal	Long	Marine shallow water-avandelta-delta-river valley			+
		Marine shallow water-hydrophyte vegetation-lagoon-beach		+	
		Shelf-beach-lagoon	0		
		Shelf-delta-valley	0		
	Short	Alluvium-ilman		0	0
		Marine shallow water-kultuk		0	0
		Lacustrine-playa		+	
		Eluvium-deluvium	+		
		"Chocolate" clay-marine shallow water		0	0
		Sequence-marine shallow water		0	0
	Mixed	Beach-deluvium-eluvium	+		
		Beach-eolian	0		
		Alluvium-eolian			0
		Marine shallow water-eolian			0

Explanation. Plus sign corresponds to present-day facies; minus sign corresponds to fossil facies.

Mixed facial sequences consist of both "foreign" and "native" facies necessarily separated by evidence of a break in sedimentation. An example is the following combination of facies: marine beach-deluvial apron-eluvium; marine beach-eolian sands.

Different regions of the Caspian coast are characterized by their own facial sequences. Dagestan shows the following combination: shelf-beach-lagoon; delta shelf-valley; eluvium-deluvium; beach of eolian sediments. The following facies sequences are characteristic of Kalmyk: marine shallow water-hydrophyte vegetation of lagoon-beach; alluvium-ilman; marine-kultuk; sequence-marine shallow water; marine sediments-eolian deposits.

The following combination of facies is found in the Volga delta: marine shallow water-avandelta-delta-river valley; alluvium-kultuk (ilman); marine shallow water-kultuk (ilman), etc.

The combination of facies (facial sequences) found in the fossil state allow us to fairly confidently reconstruct the change in depositional environment over time and also to forecast possible changes in depositional regimes as the sea level of the Caspian Sea gradually changes. At the shoaly low-lying coast, a prolonged drop in the sea level of the Caspian to -20 m absolute elevation could thus result in landward migration of the following facies sequence: shallow water-hydrophyte vegetation-lagoon-beach and, in the vicinity of Baer knolls, a shallow water-lagoon (kultuk, ilman) sequence.

* * *

Thus, a diversity of lithological composition with a predominance of sediments of the sand fractions over the area and along the section is characteristic of the latest deposits of the Caspian coast of Russia. Clays, silts, and siltstones are widely represented among the Bakin, Khazar, and Early Khvalynsk deposits of Kalmyk and the Lower Volga. Upward along the section, they are succeeded by sands of the Late Khvalynsk and New-Caspian transgressions. The opposite

pattern is observed on the coast of Dagestan, where marine Bakin and Khazar deposits of high terraces are coarser than the Khvalynsk and New-Caspian, predominantly sandy, deposits.

The facies distribution of the deposits is diverse, with aqueous (marine) formations sharply predominating. Along the section and laterally, the facies are sequences indicating definite successions and patterns of sediment deposition. Among the sediments, there are formations without facial analogs among either other fossil or present-day facies. These include the "chocolate" clay facies occurring in the lowlands of the Early Khvalynsk estuary of the Volga and the Late Khvalynsk sequence forming the Baer knolls. In the fossil state, there are no analogs of the present-day kultuk-ilman facies nor shallow water facies with abundant hydrophyte vegetation.

In large-scale features over the area and along the section, one can see a stagelike character and zonation associated with the deposition of the latest sediments on the Russian coast of the Caspian; this is due to certain features of the geological-geomorphological setting and paleogeographical evolution. In terms of lithological-mineral composition, one can distinguish broad regions of Submontane and Lowland Dagestan, Kalmyk, the Volga delta, and the Caspian aquatory.

Specific deposition features are evident in the temporal sequence of each Late Caspian transgression. The Bakin and Khazar deposits are the most differentiated over the area. "Chocolate" clays and the knoll sequence are characteristic of the Khvalynsk sediments. Sandy facies predominate among New-Caspian sediments on all coasts. Essentially coquina organogenous-terrigenous formations in areas of the floor far from the shore are especially prominent in recent sediments of the Caspian, whereas extensive areas of marine shallow water are characteristic of the lowland coasts. The shallow water areas are occupied by hydrophyte vegetation and contain huge reserves of primary organic matter. They are thus a potential source for the formation of mother beds of oil.

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VALERIY PETROVICH PETROV



Professor Valeriy Petrovich Petrov, one of our nation's greatest petrographers, a servant of science and technology in the RSFSR, doctor of geological-mineralogical sciences, and director of the Laboratory of Non-Metallic Mineral Resources of the Institute of Geology, Petrography, Mineralogy and Geochemistry of the Russian Academy of Sciences, passed on January 1, 1993 at the age of 85.

The many-sided innovative work of Valeriy Petrovich Petrov in the field of nonmetallic material resources is a testament to the broad range of his scientific interest. Already by the 1930s, he had advanced into the ranks of the most prominent petrographers-specialists in magma. The regional reports authored by him including the very extensive "Petrography of Greece" (1945, jointly with D. S. Belyankinyy), are still of major relevance. During the 1930s, one of the main directions of research pursued by V. P. Petrov became firmly established, advancing him into the circle of leading petrographers in the country. His numerous reports concerning volcanism and volcanites, intrusive rocks (labradorites to granites and pegmatites), and discovery of the interrelationship between optics and the compositions of rock-forming minerals are widely known. His handbooks "Crystal Optics" (authored jointly with D. S. Belyankinyy) and "The Immersion Method," repeatedly published in the USSR and in a number of foreign countries, was a major contribution to the development of petrographic methods of investigation. In a number of reports, during 1950-1960, the period of the "granite controversy," Valeriy Petrovich subsequently defended a concept of the origin of intrusive rocks and, together with a team of physicists, carried out a series of experiments at high temperatures and pressures to shed light on the generation of melts under abyssal conditions. In the monograph "Magma and the Genesis of Igneous Rocks" (1972), Valeriy Petrovich made history with his global conception of magmatism as a manifestation of properties of the liquid phase of the Earth, properties which are controlled by depth under conditions ranging from fresh surface waters to ultramafic melts.

During the great patriotic war, V. P. Petrov became one of the main organizers of a new raw-materials base for the fire-clay industry intrusive Urals. Patriotic duty prompted Valeriy Petrovich to requalify himself as a geologist-non-metallic mineral specialist. This was the source of a new direction in his research: an interest in ancient zones of weathering and the nonmetallic mineral resources associated with such zones. Following a detailed investigation of the Urals kaolins, extensive observations covering the territory of our country, and an analysis of world literature, V. P. Petrov put forward a number of original hypotheses, including a general concept of global epochs of vigorous weathering and

Translated from *Litologiya i Poleznye Iskopaemye*, No. 6, pp. 132-134, November-December, 1993.

periods of planetary tectonic inactivity, as well as a concept of ancient zones of weathering as fossil soils constituting a reactive envelope between the biosphere and lithosphere. This theory is gaining increasing recognition in the Commonwealth and abroad; it also has served as a reliable starting point for investigating known deposits and for directing exploration for new deposits of many mineral resources (kaolin, bauxite, sand, etc.). First presented in his doctoral dissertation published in 1948, this concept was developed and expanded by V. P. Petrov in tens of reports, including the well known monograph "Principles of Investigation of Ancient Zones of Weathering" (1967).

Since 1949, V. P. Petrov served as director of the Department of Non-Metallic Mineral Resources of the Institute of Geology, Petrography, Mineralogy and Geochemistry of the USSR. In organizing the activity of this scientific institution, he invariably and harmoniously combined theoretical and practical concerns. Studies were developed in the most practical and pressing directions and ended with the discovery of new types of commercial mineral resources and the development of new predictive-geological and technological-mineralogical approaches. Valeriy Petrovich personally spearheaded the creation of the perlite industry. In 1955, he came out in print with arguments that the time for such an industry had come and extensive estimates of perlite content of the volcanic provinces of the USSR. All of the subsequent drilling activity carried out by the perlite industry, along with the construction of tens of factories and the entrance of the USSR onto the world scene as a perlite exporter was entirely a result of the foresight of V. P. Petrov. Valeriy Petrovich took the initiative in introducing a number of new types of raw material, including high-aluminum refractory materials. Together with his co-workers and students, V. P. Petrov made recommendations for the exploitation of iron-free granites, alkaline kaolins, and porcelaneous stone as new types of ceramic raw materials. He also made recommendations for powdery talcites from zones of weathering, brucite, wollastonite, finely flaked mica, etc. He helped in the introduction of all these materials into the national economy.

The work of V. P. Petrov as a leading specialist of the country in the area of commercial nonmetallic minerals extended far beyond the small academy. He participated in volunteer planning of geological-survey and research work concerning nonmetallics, directly consulted many institutes and commercial ventures, lead all-union and international conferences, and carried out expertise work for the Commission on Resources and Deposits. Geologists-nonmetallic resource specialists gained access to knowledge concerning decorative and facing stone, asbestos, piezoelectric crystal, micas, talc, apatite, various clays, perlite, and other volcanogenic mineral resources through the articles of V. P. Petrov and the tens of monographs produced with his participation or under his editorship. The total number of printed works published by Valeriy Petrovich approaches five hundred.

His authority in all spheres of his scientific endeavor earned him a leadership role in coordinating agencies: the Council for the Study of Ore Formation (Chairman the Commission on Non-Metallics), the Petrographic Committee (Member of the Bureau), and commissions on sedimentary rocks and clays (Deputy Chairman). For many years, V. P. Petrov was an active member of the editorial board of "Izvestiya Akad. Nauk. SSSR, Seriya Geologicheskaya."

One of Valeriy Petrovich's admirable qualities was his readiness and even need to generously share his knowledge and experience. After graduating from Leningrad University in 1927, he taught for many years at a number of institutes of higher learning, conducted various courses, educated hundreds of specialists, including twenty doctoral candidates, willingly provided lectures, and published many popular-science articles and books simply and entertainingly written to satisfy curiosity. V. P. Petrov's work in geography was especially extensive. Starting with the Caucasus and Urals, he then worked in the Ukraine, in Siberia, in the Far East, and in the Kola Peninsula. He visited very different areas of our country. He brought back a wealth of interesting observations from travels to many countries on all continents. Even his brief visits invariably benefited colleagues in other countries. During a trip to Vietnam, for example, he helped in the discovery of an asbestos deposit. He opened up a deposit of alkaline kaolins in Poland and a marble deposit in Cuba. He also explained the principles of exploration for deposits associated with ancient zones of weathering, etc. in Yugoslavia, Czechoslovakia, and the former German Democratic Republic. International recognition for Valeriy Petrovich was expressed in the publication of his research in many European and Asian countries and also in the USA. He was awarded the medal of Karlov University and became a member of the London Mineralogical Society as well as the International Commission on Geological Correlation of Kaolins. As a translator and editor of translations of many fundamental works from abroad, he made an important contribution to international relations.

The extensive and many-sided contributions of Valeriy Petrovich were appreciated for their value; he was awarded three orders of "Trudovogoye Krasnogoye Znamenije," the order of "Znak Pocheta," and many medals.

Our country has lost a great investigator, a remarkable human being, and an outstanding organizer. The memory of Valeriy Petrovich Petrov will live on in our hearts.

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VITALII BORISOVICH TATARSKII



On February 27, 1993 Vitalii Borisovich Tatarskii, Professor at St. Petersburg University, Honorary Member of the All-Russian Minerological Society, outstanding student of crystallographer, lithologist, and petroleum engineer, passed away. Tatarskii had made major contributions to the development of geology.

Tatarskii worked on various problems in physical crystallography and crystal optics. The manual on crystal optics and immersion analysis which he wrote has earned universal recognition and is a standard reference work for mineralogists, petroleum engineers, lithologists, and geochemists. The presentation of the manual is distinguished by precision and conciseness of formulation, reflecting a clarity and acuity of thought.

Of particular note is the high level of knowledge we now have of the immersion method of investigation of materials, a method which its author, V. B. Tatarskii, had expended great effort on in its development and application in Russia. Tatarskii extended and the range of the immersion method with many new findings, for example, recommendations on the use of Becke stained light lines, application of a method of determining the index of refraction in small grains, the use of cleavage for diagnosis of minerals in immersion specimens, and elsewhere.

Tatarskii had been a student of Osip Markovich Ansheles, founder and director of the Department of Crystallography of Leningrad University. Succeeding Ansheles in this position, Tatarskii successfully directed the Department of Crystallography from 1958 through 1970. Though it is also somewhat unusual to say this, it must be acknowledged that the development of lithological research in our country is linked to the Department of Crystallography of Leningrad University and its chairmen, O. M. Ansheles and V. B. Tatarskii. In addition to the development of the immersion method, they also investigated sedimentary rocks and sedimentary minerals, for example, the Devonian deposits of the northwestern portion of the SNG and the Permian deposits of the Don Basin and its surroundings.

As a lithologist, V. B. Tatarskii was concerned principally with carbonate rocks and minerals, and, in particular, concentrated on the study of dolomite. His research on the genesis of dolomite has entered textbooks and manuals under the name, "Tatarskii reaction," which is understood as the theory that dolomite formed in a highly alkaline medium due to the interaction of ammonium carbonate (formed in the decomposition of organic matter with magnesium sulphate). Based on a study of the carbonate Paleogene rocks of the Tadzhik depression and the Fergan valley, Tatarskii demonstrated that Haidinger's reaction is not applicable as a means of explaining the mode of formation of stratal dolomite. He also investigated the opposite process of dedolomitization, a process that is of great practical importance.

Tatarskii created a superb handbook on the diagnosis of carbonate minerals in immersion and through the use of staining reactions. The handbook has undergone two editions (in 1952 and 1955) in the form of a separate brochure and has been widely recognized among specialists; it has been reprinted in many foreign languages.

However, his activity as a lithologist was not limited to studies of carbonate rocks and minerals. In the 1930s he undertook a detailed investigation of the pericarbonate (terrigenous) deposits of the Donets coal basin for the purpose of determining whether rock sequences could be correlated in terms of accessory minerals. Unfortunately, only brief extracts from this extensive research were published in the *Geologicheskii Zhurnal* of the Academy of Sciences of Ukraine (1934).

Tatarskii also defended a doctoral dissertation on the lithology of carbonate rocks with the title, *Petrography of the Bukhar stage of the Tadzhik depression and Certain Problems in the Petrography of Carbonate Rocks* (1952-1953).

He was interested also in determining the origin of petroleum deposits. In 1937 he completed detailed studies of oil deposits of the Fergan valley, and in 1950 published an instruction manual for petroleum workers on a technique for petrographic study of sedimentary rocks. In 1954 Tatarskii published an article in the *Vestnik* of Leningrad University on the genesis of petroleum, and in 1955 a lengthy article, entitled "On carbonate petroleum-source deposits," was published in the collection, *The Origin of Petroleum* (Gostoptekhizdat, 1955, pp. 358-405).

In these studies, Tatarskii came forth as a proponent of the hypothesis of an organic origin of petroleum and the possibility that petroleum could have been created in carbonate deposits.

For many years Tatarskii taught a course on the Petrography of Sedimentary Rocks to students in the Department of Geology of Leningrad University and also conducted other courses related to crystallography and lithology. For his achievements as a teacher, he was awarded a certificate from Leningrad University.

Vitalii Borisovich Tatarskii was a remarkable man, well-meaning and sympathetic. The following example is highly characteristic of him. When one of his foreign students was not allowed (for reasons of secrecy) to go on an expedition to collect specimens for his Candidate dissertation, Tatarskii himself went and collected the required specimens.

In taking leave of our dear colleague, we are fully justified in saying that Vitalii Borisovich Tatarskii was a prince, in the full sense of the word, in science and in life.

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ALEKSEI IVANOVICH LYASHCHENKO



Earth sciences has suffered a heavy loss: On August 23, 1992, in the his 76th year, after a severe, sudden illness, Aleksei Ivanovich Lyashchenko, outstanding lithologist, stratigrapher and paleontologist, doctor of geology and mineralogy, and Academician of the Russian National Academy of Sciences, passed away.

Lyashchenko was born March 24, 1917 in the village of Zabroda in Kharkov district into a family of peasants. He began his work life as a worker on the Armavir station of the Azov-Black Sea railroad. In 1941 he graduated with distinction from Kiev University, and went to the front as a volunteer and from 1941 to 1945 served in the ranks of the Soviet Army. He created military inventions that ended up being used at the front. A veteran of World War 2, he was awarded 13 state medals, including Orders of the Patriotic War, grades I and II.

In the postwar period Lyashchenko became a post-graduate student at the Institute of Geology of the USSR Academy of Sciences; under the direction of D. V. Nalivkin he worked on different problems related to facies and stratigraphy of the mantle of the Russian platform. His doctoral dissertation was devoted to the ecology and stratigraphy of the Devonian era; for a brief period it defined his destiny as a scientist.

For several dozen years Lyashchenko worked at the All-Russian Research Institute of Geological and Petroleum Surveys, where he successfully linked together different aspects of lithology, the stratigraphy of the Devonian era and the occurrence of oil and gas; Lyashchenko's studies in this period organically interweaved together the theory and practical application of geological surveying.

Lyashchenko's scientific activity was directed towards the development of a faunal stratigraphy of the Devonian era of the Russian platform and, basically, the analysis of groups of brachiopods. He described over 500 species and 600 genera of brachiopods, writing about them in more than half of them in various journal articles and monographs. One study of brachiopods which he conducted, and which was published in monograph form, represented a major contribution to research on this group of organisms and led to a substantial improvement in the stratigraphy of the Devonian scale. Lyashchenko personally identified over 70 stratigraphic subdivisions. He was the author of 150 studies, most of which were published, including eight monographs. His monographs on paleontology and stratigraphy have become standard reference works for specialists in the Devonian era and represent the contribution of paleontologists from around the world. A member of VAK [expansion unknown], Bureau of the Devonian Committee, All-Russian Paleontological Society, MOIP [expansion unknown], permanent active member of numerous conferences, meetings, and symposia on the stratigraphy and fauna of the Devonian era, he followed his creative and scientific path with dignity.

The name of Aleksei Ivanovich Lyashchenko, a great scientist, brilliant human being, and wonderful husband and father, will long live in the hearts of geologists throughout the world and in the hearts of his loved ones.

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(A translation of *Lithologiya i Poleznye Iskopaemye*)

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